known. Also, it is not known whether the axes through the two benzene rings are exactly parallel.) Summing up, we think that we have obtained conclusive evidence for liquid-crystalline curvature electricity and a coefficient e_{33} of reasonable sign and magnitude.

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On the Migration of Ions in Alkali Nitrate-Silver Nitrate Melts

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Stoichiometric transport numbers of the ion constituents of the molten salt mixtures $NaNO_3+AgNO_3$ and $LiNO_3+AgNO_3$ (referred to the common anion) have been determined by EMF measurements in a concentration cell with transference. The composition range is $0.7 \leqq x \leqq 1.0$ at 240 °C to $0.1 \leqq x \leqq 1.0$ at 300 °C (x denotes the mole fraction of silver nitrate) in the system $NaNO_3+AgNO_3$, and $0.1 \leqq x \leqq 1.0$ in the same temperature range in the system $LiNO_3+AgNO_3$, the phase diagram defining the lower limit and the decomposition of the melt the upper limit. In addition, ionic mobilities, conductivities, equivalent conductivities, and the characteristic quantities of the idealized melts of the two systems have been calculated at 260 °C and 290 °C.

Introduction

In 1968 SINISTRI [1] wrote: "Careful measurements of transport numbers of these systems ($NaNO_3+AgNO_3$, KNO_3+AgNO_3) would be highly desirable, . . .". At this time, measurements of these quantities by the Hittorf method existed for the system $NaNO_3+AgNO_3$ by DUKE, LAITY, and OWENS [2] and for the system KNO_3+AgNO_3 by DUKE and OWENS [3]. These measurements "are scanty and somewhat uncertain" (SINISTRI [1]). Since then the work of OKADA and KAWAMURA [4] has been published; these authors determined the transport numbers for KNO_3+AgNO_3 at 300 °C by EMF measurements in a concentration cell with transference. The electrodes of this cell were two nitrate electrodes as developed by KETELAAR and DAMMERS-DEKLERK [5]. The transport numbers of Okada and Kawamura agree very well with those of Duke and Owens.

The purpose of this paper is the determination of the stoichiometric transport numbers of the ion constituents in the systems $NaNO_3+AgNO_3$ and $LiNO_3+AgNO_3$ by EMF measurements in a concentration cell with transference, as functions of composition and temperature. The activity coefficients required for the analysis were also obtained in our laboratory [6] from EMF measurements in a chemical cell containing a nitrate electrode of the type cited above [5]. Thus the uniformity of the experimental methods and of the possible errors are guaranteed. The transport numbers of the system $NaNO_3+AgNO_3$ determined here can be compared to those of DUKE, LAITY, and OWENS [2] and of AZIZ and WETMORE [7]. The transport numbers of the system $LiNO_3+AgNO_3$ can be confronted with those of KAWAMURA and OKADA [8] recently published.

The ionic mobilities and conductivities of the ion constituents and the equivalent conductivities of the two systems follow from the transport numbers and from the densities and electrical conductivities of the mixtures. The equivalent conductivities and the transport numbers of the idealized melts can be calculated from these ionic conductivities.

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Theory

The formulae derived in the following hold for molten salts consisting of two components with a common cation or anion. We choose the following nomenclature: The ion constituent occurring in component 1 only will be denoted by a, the ion constituent occurring in component 2 only will be denoted by b, and the ion constituent common to both components by c (i = a, b, c). This means for the system $NaNO_3 + AgNO_3$: $a = Na^+$, $b = Ag^+$, $c = NO_3^-$; for the system $LiNO_3 + AgNO_3$: $a = Li^+$, $b = Ag^+$, $c = NO_3^-$.

The stoichiometric transport number t_i of the ion constituent i referred to the velocity $\boldsymbol{v}_c$ of the common ion constituent c is defined by

$$t_i = \frac{z_i\, c_i\, (\boldsymbol{v}_i - \boldsymbol{v}_c)}{\sum\limits_i z_i\, c_i\, \boldsymbol{v}_i} \tag{1}$$

where z_i denotes the charge number, c_i the molar concentration, and $\boldsymbol{v}_i$ the velocity of the ion constituent i.

The transport numbers can be derived from the EMF of a concentration cell with transference indicated in the following form:

$$\begin{aligned}&\mathrm{Cu} \mid \mathrm{Ag} \mid NaNO_3 + AgNO_3\,(x_I) \mid \\ &\quad \cdot \mid NaNO_3 + AgNO_3\,(x_{II}) \mid \mathrm{Ag} \mid \mathrm{Cu}\end{aligned} \tag{2}$$

and

$$\begin{aligned}&\mathrm{Cu} \mid \mathrm{Ag} \mid LiNO_3 + AgNO_3\,(x_I) \mid \\ &\quad \cdot \mid LiNO_3 + AgNO_3\,(x_{II}) \mid \mathrm{Ag} \mid \mathrm{Cu}\,.\end{aligned} \tag{3}$$

The copper wires (Cu) are the terminals connecting the silver electrodes (Ag) with the electrical instruments. The sign $\mid\mid$ symbolizes the liquid junction, and x_I and x_{II} are the mole fractions of silver nitrate in the half cell on the left (I) and the right (II), respectively. By definition, x_I indicates the standard composition, which may refer to pure silver nitrate. x_{II} is the variable composition. However, there will be convection for great differences in composition ($x_{II} < x_I$), due to the differences in the densities of the two mixtures. Therefore, we prefer to choose a smaller value of x_I, that is to say, a mixture instead of the pure salt. The new reference composition will be denoted by the symbol x_I'. We then merely have to add the measured EMF to the value of the cell

$$\begin{aligned}&\mathrm{Cu} \mid \mathrm{Ag} \mid NaNO_3 + AgNO_3\,(x_I) \mid \\ &\quad \cdot \mid NaNO_3 + AgNO_3\,(x_I') \mid \mathrm{Ag} \mid \mathrm{Cu}\,.\end{aligned} \tag{4}$$

The two electrodes are reversible to silver ions.

HAASE and RICHTER [9] have given the general formula for the EMF (Φ) of the isothermal-isobaric cell of type (2) or (3):

$$F\,\Phi = R\,T \int\limits_{x_I}^{x_{II}} \frac{z_a\,\nu_a\,(1-x) + z_b\,\nu_b\,x}{z_a\,z_b\,\nu_a\,\nu_b\,(1-x)}\; t_a \,\mathrm{d}\ln a_2\,. \tag{5}$$

R denotes the gas constant, T the thermodynamic temperature, ν_i is the stoichiometric number of the ion constituent i, x denotes the mole fraction and a_2 the activity of component 2 (silver nitrate).

For molten salts consisting of two uni-univalent electrolytes we find for the activity of component 2 that [10]

$$a_2 = x\,f_2\,, \tag{6}$$

where f_2 denotes the activity coefficient of component 2.

With $z_a = z_b = 1$, $\nu_a = \nu_b = 1$ and with Eq. (6) we get from Eq. (5)

$$F\,\Phi = R\,T \int\limits_{x_I}^{x_{II}} \frac{1}{1-x}\; t_a \,\mathrm{d}\ln (x\,f_2)\,. \tag{7}$$

Equation (7) is the formula of the measurable EMF of cell (2) or (3), composed of two immeasurable electrode potentials and the diffusion potential. The unambiguity of the electromotive force of the cells investigated was proven earlier [11].

By differentiation of Eq. (7) with respect to the upper limit we obtain

$$t_a = (1 - x_{II}) \cdot [\mathrm{d}\tau / \mathrm{d}\ln (x\,f_2)]\,, \tag{8}$$

where τ denotes $\tau \equiv F\,\Phi / R\,T$. From Eq. (8) we get t_a ($a = Na^+, Li^+$) and with the identity $\sum\limits_i t_i = 1$ and the definition $t_c \equiv 0$, following from Eq. (1), we obtain the transport number of the silver ion t_b:

$$t_b = 1 - t_a\,. \tag{9}$$

Starting from these transport numbers and from the well-known densities and electric conductivities $\varkappa$, we calculate the ionic mobilities u_i of ion constituent i (referred to the common anion):

$$u_a = \frac{t_a\,\varkappa\,\overline{V}}{F\,z_a\,\nu_a\,(1-x)}\,, \qquad u_b = \frac{t_b\,\varkappa\,\overline{V}}{F\,z_b\,\nu_b\,x}\,, \tag{10}$$

where $\overline{V}$ denotes the molar volume of the mixture.

For the equivalent conductivity Λ as defined by TIMMERMANN and RICHTER [12] we have

$$\Lambda = (1-x)\,\lambda_a + x\,\lambda_b\,. \tag{11}$$

λ_i is the ionic conductivity of ion constituent i referred to the common anion

$$\lambda_a = F \cdot u_a\,, \qquad \lambda_b = F \cdot u_b\,. \tag{12}$$

We define the limiting values

$$\lim_{x \to 0} \Lambda \equiv \Lambda_1^{\bullet} = \lambda_a^{\bullet}, \quad \lim_{x \to 1} \Lambda \equiv \Lambda_2^{\bullet} = \lambda_b^{\bullet}, \tag{13}$$

where $\lambda_a^{\bullet}$ and $\lambda_b^{\bullet}$ denote the ionic conductivities of the ion constituent a in the pure component 1 and of the ion constituent b in the pure component 2, respectively. We also define

$$\lim_{x \to 1} \lambda_a \equiv \lambda_a^{\infty(2)}, \qquad \lim_{x \to 0} \lambda_b \equiv \lambda_b^{\infty(1)}, \tag{14}$$

where $\lambda_a^{\infty(2)}$ is the ionic conductivity of a at infinite dilution in component 2 and $\lambda_b^{\infty(1)}$ the analogous quantity for b. We thus obtain as the condition for an "idealized melt":

$$\lambda_i = \lambda_i^{\bullet} = \lambda^{\infty} \quad (i = a, b)\,. \tag{15}$$

The equivalent conductivity of the idealized melt is

$$\Lambda^{id} = (1 - x)\, \lambda_a^{\bullet} + x\, \lambda_b^{\bullet}. \tag{16}$$

The corresponding transport numbers are

$$t_a^{id} = (1 - x)\, \lambda_a^{\bullet} / \Lambda^{id}, \quad t_b^{id} = x\, \lambda_b^{\bullet} / \Lambda^{id}. \tag{17}$$

The idealized melt is characterized by Eqs. (16) and (17), and the excess function of the equivalent conductivity given by

$$\Lambda^E = \Lambda - \Lambda^{id}\,. \tag{18}$$

Experimental

EMF measurements on a concentration cell with transference may be carried out rather precisely for molten salts. In the literature, however, there are only descriptions of such cells containing a porous disk, a membrane, silica powder, or something similar; there is no consideration of the fact that thus another component may be introduced into the system. In this work the transference was established by a direct liquid junction of the molten salts. Thus the formulae given here hold rigorously.

The apparatus, in principle, consisted of a Duran-glass cell, two silver electrodes, a compensator in the usual compensation circuit, an automatically working compensation recorder, and a furnace and the corresponding controller.

The cell (Fig. 1) consists of the two electrode compartments A_1 and A_2 and of the center compartment B, in which the transference is made by overpressure of the protective gas (nitrogen) without a porous membrane. The standpipe S renders possible the pressure balancing during the filling of the cell with the salts and during the changing of the level of the melts in A_1 and A_2 when the liquid junction is established. The overpressure is adjusted by the tube R, which is movable in a water vessel.

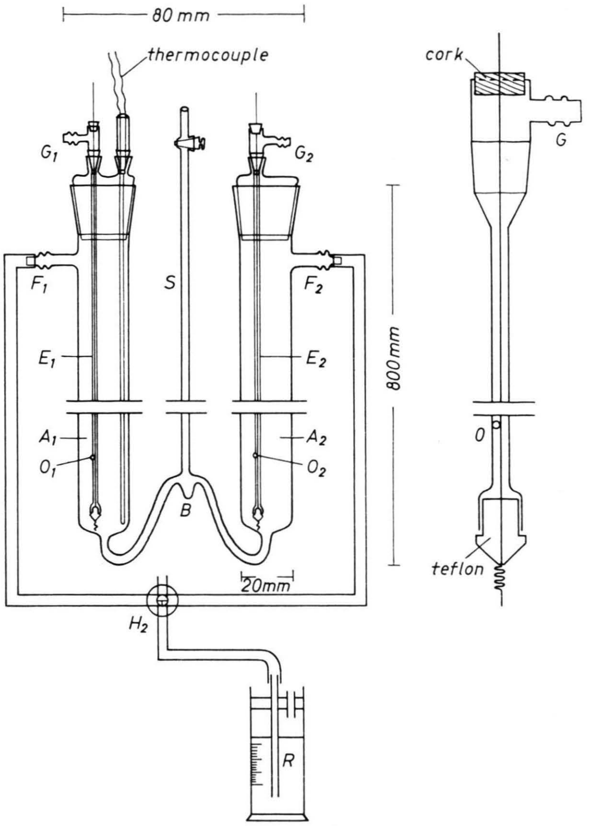

Fig. 1. Concentration cell with transference and electrodes.

The electrodes E_1 and E_2 are fixed about 3 cm above the cell bottom. The electrodes consist of a silver wire ($\diameter$ 1 mm) in Duran glass tubes. They are held at the bottom by a teflon seal, at the top by a cork stopper (Fig. 1). The glass tube of the electrodes is simultaneously the gas inlet. The nitrogen coming over G_1 and G_2 in the apparatus arrives at the free cell volume through O_1 and O_2 slightly above the melt. The protective gas can leave the apparatus through the openings F_1 and F_2, when the three-way stopcock H_2 is in the right position.

The EMF of the cell was stable for at least 72 hours for all measurements. This corresponds to the measuring time of the longest series of experiments. The asymmetry potential of the electrodes was determined in each experiment and was always very small ($\Delta\Phi < 0.03$ mV). It was neglected in the analysis of the measurements.

The assembly was located in a cylindrical furnace specially fabricated for these experiments.

The EMF was measured by a compensator of Feussner in a compensation circuit and was recorded by an automatically working compensation recorder. In the same way, the thermoelectric potential of the thermocouple was measured, which determines the temperature of the melt close to one silver electrode[13].

Results and Discussion

In Table 1, the measured EMF values for the system $NaNO_3 + AgNO_3$ referred to pure silver nitrate are presented. In Table 2, the corresponding values for the system $LiNO_3 + AgNO_3$ as a function of composition at several temperatures are tabulated.

Based on the phase diagram[14], 240 °C was chosen as the lower temperature limit for the system $NaNO_3 + AgNO_3$, at which it still can be measured in the concentration range $0.7 \leqq x \leqq 1.0$. At 300 °C, it can be measured in the concentration range $0.1 \leqq x \leqq 1.0$. Thermal decomposition is observable above 320 °C, especially in melts rich in silver nitrate. Thus 300 °C was chosen as the upper temperature limit. For similar reasons (phase diagram[15]), we measure the EMF for the system $LiNO_3 + AgNO_3$ in the composition ranges $0.15 \leqq x \leqq 1.0$ at 240 °C and $0.1 \leqq x \leqq 1.0$ at 300 °C.

The stoichiometric transport numbers follow from Eqs. (8) and (9), taking account of the EMF values and the activity coefficients measured in our laboratory[6]. The differential quotient $d\tau / d \ln (x f_2)$ was determined graphically rather accurately.

In Table 3, the transport number of the silver ion in the system $NaNO_3 + AgNO_3$ is given as a function of composition and temperature. In Table 4, the corresponding values for the system $LiNO_3 + AgNO_3$ are tabulated.

The temperature dependence of the activity coefficients f_2 of component 2 in both investigated

Table 1. $NaNO_3+AgNO_3$: EMF (Φ), referred to pure silver nitrate, as a function of composition and temperature.

x	$-\Phi \cdot 10^3/V$ 240°C	250°C	260°C	270°C	280°C	290°C	300°C
0.95	1.51	1.55	1.59	1.63	1.67	1.72	1.76
0.90	3.10	3.18	3.26	3.34	3.42	3.50	3.58
0.85	4.82	4.94	5.07	5.20	5.32	5.46	5.58
0.80	6.78	6.97	7.16	7.35	7.53	7.72	7.91
0.70	10.80	11.10	11.40	11.70	12.00	12.30	12.60
0.65		13.50	13.80	14.10	14.40	14.70	15.00
0.60		15.96	16.39	16.80	17.23	17.66	18.09
0.50				22.96	23.88	24.81	25.73
0.40					30.40	31.86	33.82
0.30						40.01	41.81
0.20							55.23
0.15							67.04
0.10							80.71

Table 2. $LiNO_3+AgNO_3$: EMF (Φ), referred to pure silver nitrate, as a function of composition and temperature.

x	$-\Phi \cdot 10^3/V$ 240°C	250°C	260°C	270°C	280°C	290°C	300°C
0.90	2.40	2.42	2.45	2.50	2.55	2.60	2.65
0.80	5.20	5.25	5.40	5.50	5.60	5.70	5.80
0.75	6.60	6.77	6.94	7.11	7.28	7.45	7.62
0.70	8.20	8.40	8.60	8.80	9.00	9.20	9.40
0.60	11.50	11.99	12.20	12.61	12.80	13.23	13.40
0.55	13.42	13.78	14.14	14.50	14.86	15.22	15.58
0.50	15.44	15.87	16.40	16.74	17.17	17.60	18.03
0.45	18.00	18.40	19.00	19.50	20.00	20.50	20.80
0.40	21.00	21.50	22.15	22.67	23.19	23.71	24.23
0.35	24.60	25.25	25.90	26.50	27.20	27.75	28.30
0.30	29.02	29.74	30.45	31.18	31.90	32.62	33.20
0.25	34.00	34.79	35.59	36.39	37.20	38.00	38.80
0.20	39.75	40.74	41.72	42.70	43.69	44.68	45.67
0.15	51.95	53.19	54.44	55.74	57.00	58.25	59.50
0.10		71.09	72.75	74.43	76.15	77.82	79.49

Table 3. $NaNO_3+AgNO_3$: Transport number t_b of the silver ion referred to the common nitrate ion as a function of composition and temperature.

x	t_b 240°C	250°C	260°C	270°C	280°C	290°C	300°C
0.95	0.97	0.97	0.97	0.96	0.96	0.96	0.95
0.90	0.93	0.93	0.93	0.92	0.91	0.90	0.89
0.85	0.89	0.87	0.87	0.86	0.84	0.83	0.83
0.80	0.83	0.79	0.80	0.79	0.76	0.76	0.76
0.70	0.64	0.59	0.56	0.60	0.64	0.62	0.64
0.65		0.49	0.48	0.52	0.58	0.56	0.57
0.60		0.38	0.40	0.48	0.51	0.49	0.49
0.50				0.46	0.48	0.46	0.45
0.40					0.47	0.45	0.44
0.30						0.37	0.35
0.20							0.25

Table 4. $LiNO_3+AgNO_3$: Transport number t_b of the silver ion referred to the common nitrate ion as a function of composition and temperature.

x	t_b 240°C	250°C	260°C	270°C	280°C	290°C	300°C
0.90	0.96	0.96	0.96	0.95	0.95	0.95	0.95
0.80	0.89	0.89	0.89	0.88	0.88	0.89	0.88
0.75	0.85	0.85	0.85	0.84	0.84	0.85	0.85
0.70	0.80	0.80	0.81	0.80	0.80	0.81	0.81
0.60	0.68	0.69	0.70	0.71	0.71	0.72	0.73
0.55	0.61	0.63	0.64	0.65	0.65	0.67	0.68
0.50	0.55	0.56	0.57	0.59	0.59	0.60	0.62
0.45	0.48	0.49	0.49	0.53	0.53	0.54	0.55
0.40	0.41	0.42	0.43	0.46	0.46	0.47	0.47
0.35	0.35	0.36	0.37	0.39	0.40	0.40	0.40
0.30	0.29	0.30	0.31	0.32	0.33	0.32	0.32
0.25	0.22	0.23	0.23	0.24	0.24	0.23	0.24
0.20	0.15	0.15	0.15	0.16	0.16	0.15	0.15
0.15	0.10	0.10	0.09	0.10	0.10	0.09	0.09
0.10		0.05	0.05	0.05	0.05	0.05	0.05

systems is given by RICHTER and SEHM[6] by

$$R \ln f_2 = (A/T) + B\,. \tag{19}$$

The coefficients A and B still depend on x. For the temperature dependence of the EMF measured in this work, we find linear behaviour:

$$\Phi = C + D\,T. \tag{20}$$

C and D also depend on x. From Eq. (19) and Eq. (20) it follows for the differential quotient $\mathrm{d}\tau/\mathrm{d}\ln(x\,f_2)$ in Eq. (8) that

$$\frac{\mathrm{d}(F/R)\,[C/T+D]}{(A/R)\,\mathrm{d}(1/T)} = \frac{F\,C}{A}\,. \tag{21}$$

Comparison of Eq. (21) with (8) gives:

$$t_a = (1 - x_{\mathrm{II}})\,F\,C/A\,. \tag{22}$$

Thus the transport numbers of the ion constituents in the systems $NaNO_3+AgNO_3$ and $LiNO_3+AgNO_3$ do not depend on temperature. This is confirmed by the data of Tables 3 and 4, respectively, within the accuracy of the measurements and the graphical differentiation.

The transport numbers of the silver ion in the system $NaNO_3+AgNO_3$ at 290 °C, together with those of DUKE et al.[2] at 305 °C, are plotted in Figure 2. There is a distinct deviation of our results (solid line) from the linear dependence of the transport number on the mole fraction, which was found by Duke et al. with the Hittorf method (dashed line). We think that our results are more reliable. The temperature control quoted as ±5 °C by Duke et al. is now essentially improved (±1 °C), in the EMF method there is no concentration analysis *after* the experimental run, and there is no membrane in the EMF cell, as used by Duke et al. in the Hittorf cell. The EMF method permits the temperature to

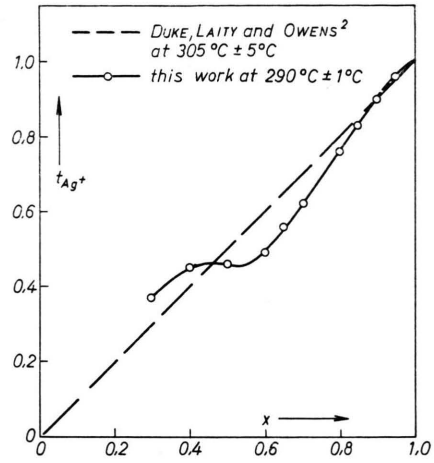

Fig. 2. $NaNO_3+AgNO_3$: Transport number of the silver ion as a function of the mole fraction x of silver nitrate.

be varied without additional effort, so that measurements in the whole temperature range were possible, only subjected to the restrictions due to the phase diagram and decomposition of the melt.

AZIZ and WETMORE[7] determined t_b of the silver ion in the system $NaNO_3+AgNO_3$ at 330 °C in the composition range $0.05 \leqq x \leqq 0.25$. In this small composition range, our transport numbers agree well with those of Aziz and Wetmore.

In Fig. 3, we plot the transport numbers of the silver ion in the system $LiNO_3+AgNO_3$ at 260 °C, along with those of KAWAMURA and OKADA[8] at 300 °C. There is again a discrepancy between our results (solid line) and those obtained with the Hittorf method by Kawamura and Okada (dashed line), and for the same reasons as above we think that our results are more reliable. They measured at 5 concentrations across the whole composition range for 2 temperatures (300 °C and 350 °C), while our results were determined at 15 concentrations across the whole range for 7 temperatures. The experimental temperature of 350 °C seems to be too high, in view of the decomposition of the melt. Kawamura and Okada also found that the transport numbers are independent of temperature, within experimental accuracy, except at one composition (probably an effect of the decomposition mentioned above).

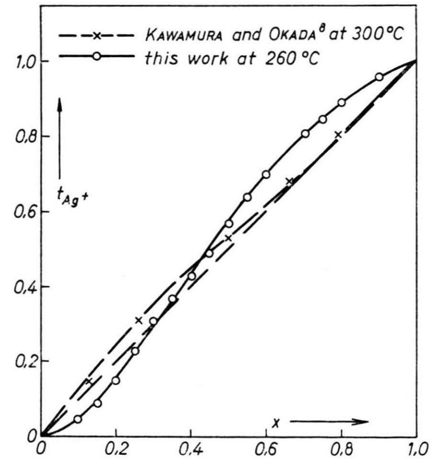

Fig. 3. $LiNO_3+AgNO_3$: Transport number of the silver ion as a function of the mole fraction x of silver nitrate.

We calculated the ionic mobilities from these transport numbers by means of Eq. (10). The densities of the mixtures $NaNO_3+AgNO_3$ have been measured by BYRNE, FLEMING, and WETMORE[16] at various temperatures, and the electric conductivities by the same authors[16] and by DE NOOIJER[17]. The densities of the mixtures of $LiNO_3+AgNO_3$ have been measured by BRILLANT[18], and the electric conductivities by BRILLANT[18] and by BYRNE, FLEMING, and WETMORE[16]. From the ionic mobilities, we obtained with Eq. (12) the ionic conductivities and from Eq. (11), or from the relation $\Lambda=\varkappa \overline{V}$, the equivalent conductivity.

The calculated quantities are given here for 290 °C in the system $NaNO_3+AgNO_3$ (Table 5) and for 260 °C in the system $LiNO_3+AgNO_3$ (Table 6). (For the values at the other temperatures see Ref. [13]). The curves of λ_a, λ_b, and Λ for the two systems at these temperatures are given in Fig. 4 and 5, respectively. At present, we are mea-

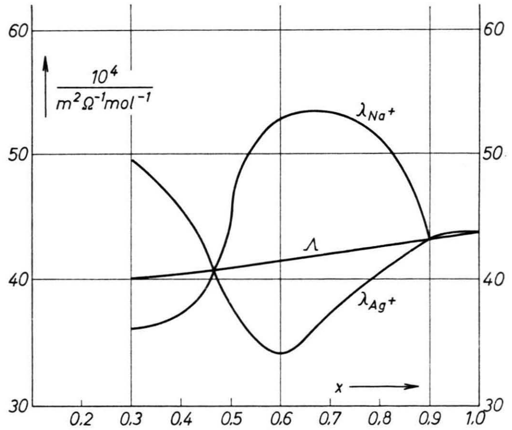

Fig. 4. $NaNO_3+AgNO_3$: Ionic conductivities λ_{Na^+} and λ_{Ag^+} and equivalent conductivity Λ as functions of the mole fraction x of silver nitrate at 290 °C.

Table 5. $NaNO_3+AgNO_3$: Electric conductivity $\varkappa$, molar volume $\overline{V}$, ionic conductivities λ_{Na^+} and λ_{Ag^+}, ionic mobilities u_{Na^+} and u_{Ag^+}, and equivalent conductivity Λ as functions of composition at 290 °C.

x	$\varkappa \cdot 10^{-2}$ $\Omega^{-1}\,m^{-1}$	$V \cdot 10^3$ $dm^3\,mol^{-1}$	$\lambda_{Na^+} \cdot 10^4$ $m^2\,\Omega^{-1}\,mol^{-1}$	$\lambda_{Ag^+} \cdot 10^4$ $m^2\,\Omega^{-1}\,mol^{-1}$	$u_{Na^+} \cdot 10^8$ $m^2\,V^{-1}\,s^{-1}$	$u_{Ag^+} \cdot 10^8$ $m^2\,V^{-1}\,s^{-1}$	$\Lambda \cdot 10^4$ $m^2\,\Omega^{-1}\,mol^{-1}$
1.0	1.0032	43.740	—	43.88	—	4.55	43.88
0.9	0.9900	43.804	43.37	43.37	4.49	4.49	43.37
0.8	0.9768	43.876	51.43	40.72	5.33	4.22	42.86
0.7	0.9615	43.930	53.50	37.41	5.54	3.88	42.24
0.6	0.9482	43.990	53.18	34.06	5.51	3.53	41.71
0.5	0.9345	44.036	44.44	37.86	4.60	3.92	41.15
0.4	0.9219	44.106	37.27	45.74	3.86	4.74	40.66
0.3	0.9115	44.186	36.25	49.67	3.76	5.15	40.28

Table 6. $LiNO_3+AgNO_3$: Electric conductivity $\varkappa$, molar volume $\overline{V}$, ionic conductivities λ_{Li^+} and λ_{Ag^+}, ionic mobilities u_{Li^+} and u_{Ag^+}, and equivalent conductivity Λ as functions of composition at 260 °C.

x	$\varkappa\ 10^{-2}$ $\Omega^{-1}\,m^{-1}$	$\overline{V} \cdot 10^3$ $dm^3\,mol^{-1}$	$\lambda_{Li^+} \cdot 10^4$ $m^2\,\Omega^{-1}\,mol^{-1}$	$\lambda_{Ag^+} \cdot 10^4$ $m^2\,\Omega^{-1}\,mol^{-1}$	$u_{Li^+} \cdot 10^8$ $m^2\,V^{-1}\,s^{-1}$	$u_{Ag^+} \cdot 10^8$ $m^2\,V^{-1}\,s^{-1}$	$\Lambda \cdot 10^4$ $m^2\,\Omega^{-1}\,mol^{-1}$
1.0	0.8740	43.371	—	37.91	—	3.93	37.91
0.9	0.8660	42.885	14.86	39.62	1.54	4.10	37.14
0.8	0.8600	42.467	20.09	40.63	2.08	4.21	36.52
0.7	0.8620	41.986	22.92	41.88	2.37	4.34	36.19
0.6	0.8550	41.429	26.57	41.32	2.75	4.28	35.42
0.5	0.8496	41.021	29.97	39.73	3.10	4.12	34.85
0.4	0.8474	40.503	32.60	36.89	3.38	3.82	34.32
0.3	0.8437	40.074	33.33	34.94	3.45	3.62	33.81
0.2	0.8379	39.614	35.26	24.89	3.65	2.58	33.19
0.1	0.8327	39.049	34.33	16.26	3.56	1.68	32.52
0.0	0.8250	38.515	31.77	—	3.29	—	31.77

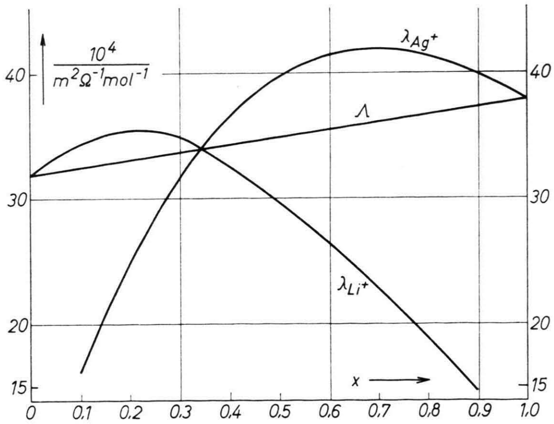

Fig. 5. ʼ$LiNO_3+AgNO_3$: Ionic conductivities λ_{Li^+} and λ_{Ag^+} and equivalent conductivity Λ as functions of the mole fraction x of silver nitrate at 260 °C.

suring the diffusion coefficients for these systems at the same temperatures.

The ionic conductivities and the equivalent conductivity increase with increasing temperature in the whole range of compositions. For both systems, the equivalent conductivity is a linear function of composition at any temperature.

The ionic conductivity of the silver ion and the sodium ion in Fig. 4 passes through a minimum and maximum, respectively. At the limit of pure silver nitrate ($x \to 1$), the ionic conductivity $\lambda_b^{\cdot}$ of the silver ion is identical with the equivalent conductivity of the system [see Eq. (13)], and the ionic conductivity λ_a of the sodium ion reaches the limiting value $\lambda_a^{\infty(2)}$ [see Eq. (14)]. The ionic conductivities of the system $LiNO_3 + AgNO_3$ (Fig. 5) show analogous behaviour.

We can calculate Λ^{id} from Eq. (16), using the limiting values (13). Λ and Λ^{id} give identical straight lines, within experimental accuracy. Therefore we need no graph for Λ^E [Eq. (18)], which would only be a measure of this accuracy. This does not mean that the systems are idealized melts, for Eq. (15) is not satisfied. We made an attempt at an explanation elsewhere [12].

The transport numbers of the idealized melt, which do not depend on temperature, were calculated by Eq. (17) and are summarized in Table 7 for the system $NaNO_3 + AgNO_3$. According to Eq. (17), t_b^{id} is the same for both systems and thus, on account of Eq. (9), t_a^{id} as well. In Fig. 6 t_b^{id} for the system $NaNO_3 + AgNO_3$ is plotted together with the measured t_b. We see that the deviation of t_b from t_b^{id} is much more apparent than the deviation of Λ from Λ^{id}.

Table 7. $NaNO_3 + AgNO_3$: Transport number t_{Na+}^{id} of the sodium ion and t_{Ag+}^{id} of the silver ion in the idealized melt as functions of composition ($\lambda_{Ag+} = 43.88 \cdot 10^{-4}\ m^2\ \Omega^{-1}\ mol^{-1}$, $\lambda_{Na+} = 39.00 \cdot 10^{-4}\ m^2\ \Omega^{-1}\ mol^{-1}$).

x	t_{Na+}^{id}	t_{Ag+}^{id}
1.0	0.00	1.00
0.9	0.09	0.91
0.8	0.18	0.82
0.7	0.27	0.73
0.6	0.37	0.63
0.5	0.47	0.53
0.4	0.57	0.43
0.3	0.67	0.33

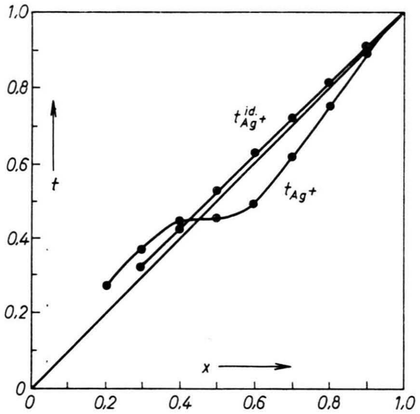

Fig. 6. $NaNO_3 + AgNO_3$: Transport number and idealized transport number of the silver ion as functions of the mole fraction x of silver nitrate.

Figure 6 shows distinctly that the system $NaNO_3 + AgNO_3$ does not meet the requirements of an idealized melt, though at first sight it might seem so in view of the behaviour of Λ and Λ^{id}. The linearity of Λ and Λ^{id} is only a consequence of a compensation effect we discussed in another paper[12]. The same holds for the system $LiNO_3 + AgNO_3$.

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