Internal Cation Mobilities in Molten (Li, Ag)NO_3 and (K, Ag)NO_3 Remeasured by the Klemm Method

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Z. Naturforsch. **47a**, 781–787 (1992); received January 21, 1992

Internal mobility ratios b_{Li}/b_{Ag} and b_K/b_{Ag} in molten (Li, Ag)NO_3 and (K, Ag)NO_3 have been measured by Klemm's countercurrent electromigration method. From these and available data on the densities and conductivities the internal mobilities have been calculated. The present experiments yielded more accurate data than previous ones using other methods. Over the investigated range of concentration and temperature, b_{Ag} is greater than b_{Li} or b_K. The results are discussed together with earlier ones obtained for (Na, Ag)NO_3.

Introduction

In [1] we measured the ratio of the cation internal mobilities in the molten system (Na, Ag)NO_3 at five temperatures by Klemm's countercurrent electromigration method and calculated the internal mobilities. The isotherms thus obtained are considerably different from those obtained with other methods. Since the Klemm method probably yields the most reliable data on internal mobility ratios among available methods, it was thought worthwhile to remeasure also the ratios in molten (Li, Ag)NO_3 and (K, Ag)NO_3 and to compare the results with those for (Na, Ag)NO_3.

Experimental

Reagent grade $AgNO_3$, $LiNO_3$ and KNO_3 were used. The apparatus and procedures used were similar to those in the previous study [1].

Results

The relative difference in the internal mobilities is defined as

$$\varepsilon_{Alk\,Ag} = (b_{Alk} - b_{Ag})/b, \tag{1}$$

where

$$b = x_{Alk}\, b_{Alk} + x_{Ag}\, b_{Ag}. \tag{2}$$

Here, x_a is the mole fraction of the salt with the cation a ($x_{Alk} + x_{Ag} = 1$).

The ε values obtained for the two systems are listed in Tables 1 and 2, together with the main experimental conditions.

The b_{Alk} and b_{Ag} are calculated from ε, the conductivity and the density by the equations given in [1], the

Table 1. The relative difference in the internal mobilities in (Li, Ag)NO_3. The sign ± for x_{Ag} and ε indicates the errors due to the chemical analysis. Q is the charge transported during the duration t of the run.

Exp. no.	T/K	x_{Ag}	Q/C	t/h	ε
1	523	0.100±0.001	1120	4.3	−0.123±0.005
2		0.302±0.003	1093	3.4	−0.125±0.006
3		0.510±0.003	1119	4.2	−0.138±0.004
4		0.700±0.006	1094	3.6	−0.140±0.010
5		0.901±0.008	1060	3.6	−0.168±0.029
6	543	0.098±0.001	1113	3.5	−0.114±0.010
7		0.302±0.003	1117	3.6	−0.116±0.005
8		0.494±0.004	1141	3.5	−0.121±0.008
9		0.696±0.007	1108	3.6	−0.129±0.010
10		0.900±0.008	1120	3.9	−0.148±0.025
11	563	0.099±0.001	1118	4.1	−0.101±0.006
12		0.304±0.002	1108	4.0	−0.121±0.005
13		0.514±0.003	1215	4.5	−0.123±0.005
14		0.704±0.009	1131	4.0	−0.131±0.015
15		0.897±0.009	1076	5.3	−0.167±0.040
16	583	0.101±0.001	1112	4.1	−0.125±0.007
17		0.300±0.002	1129	3.8	−0.118±0.004
18		0.523±0.003	1278	4.8	−0.118±0.006
19		0.705±0.005	1197	4.0	−0.134±0.009
20		0.897±0.009	1097	4.8	−0.126±0.035
21	603	0.097±0.001	1288	4.5	−0.115±0.009
22		0.298±0.003	1264	4.2	−0.102±0.007
23		0.513±0.003	1201	4.8	−0.115±0.004
24		0.697±0.006	1128	4.4	−0.122±0.009
25		0.900±0.009	1043	4.0	−0.134±0.042

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data on the conductivities and densities of the two systems being taken from [2, 3].

The calculated internal mobilities are given in Tables 3 and 4, and the corresponding isotherms are shown in Figs. 1 and 3. For comparison, in Fig. 2 the results obtained in [1] for (Na, Ag)NO_3 are shown.

Comparison with results obtained with other methods

For the system (Li, Ag)NO_3, five original papers report measurements of the cation mobility ratios (see Table 5).

Kawamura [4] used the Hittorf method. Kawamura and M. Okada [5] later found that in [4] there had been some mistakes in the gravimetric analyses of the Li^+ content and remeasured the ratios by the same method using a silver anode. Subsequently, they [6] also employed the EMF method of type A [7] to measure the ratio; type A refers to the method in which inert electrodes surrounded by nitrous gas are used. The agreement between [5] and [6] was satisfactory, though the experimental error of some measurements in [5] was large.

Richter and Amkreutz [8] employed the EMF method of type B [7]; type B refers to the EMF method where silver electrodes are used.

Table 2. The relative difference in the internal mobilities in (K, Ag)NO_3. See also the legend of Table 1.

Exp. no.	T/K	x_{Ag}	Q/C	t/h	ε
101	543	0.503 ± 0.001	888	4.0	−0.221 ± 0.003
102		0.711 ± 0.001	888	4.0	−0.234 ± 0.003
103		0.882 ± 0.000	891	4.0	−0.231 ± 0.000
104	583	0.305 ± 0.002	1196	4.3	−0.180 ± 0.004
105		0.496 ± 0.001	897	4.0	−0.180 ± 0.003
106		0.700 ± 0.001	988	3.5	−0.182 ± 0.003
107		0.899 ± 0.004	1037	3.8	−0.181 ± 0.002
108	623	0.106 ± 0.003	1317	4.5	−0.107 ± 0.008
109		0.209 ± 0.003	1089	4.0	−0.153 ± 0.004
110		0.505 ± 0.004	1313	5.0	−0.147 ± 0.005
111		0.703 ± 0.001	1112	3.9	−0.164 ± 0.002
112		0.900 ± 0.000	1107	3.9	−0.179 ± 0.003

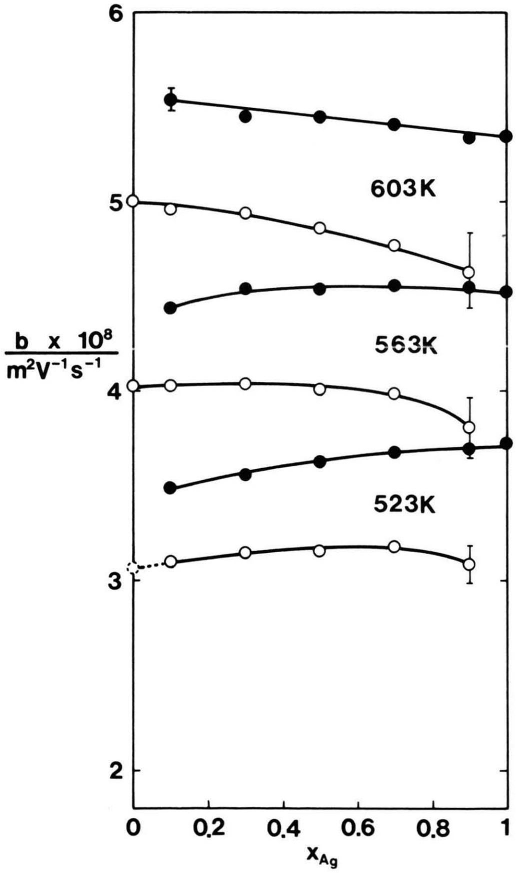

Fig. 1. Internal mobilities in (Li, Ag)NO_3. ○: Li, ●: Ag; ◌: b_{Li} extrapolated with respect to temperature.

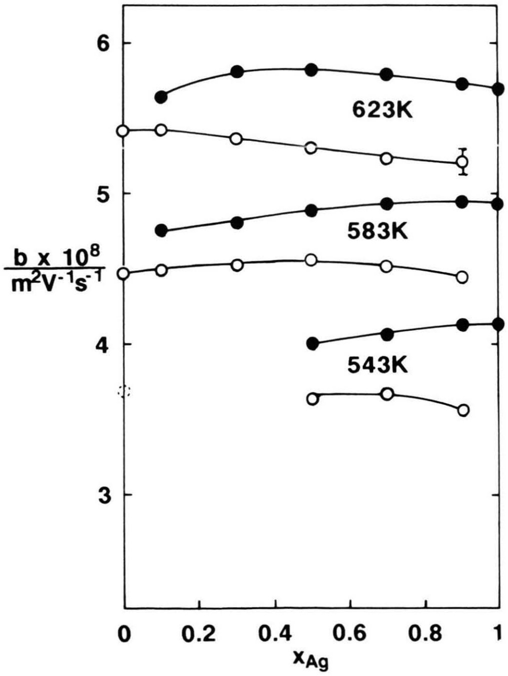

Fig. 2. Internal mobilities in (Na, Ag)NO_3 [1]. ○: Na, ●: Ag; ◌: b_{Na} extrapolated with respect to temperature.

Table 3. Internal mobilities b_{Li} and b_{Ag}. The errors given are those due only to ε.

Exp. no.	T (K)	x_{Ag}	$\varkappa$ (10^2 S m^{-1})	V (10^{-6} m^3 mol^{-1})	b_{Li} (10^{-8} m^2 V^{-1} s^{-1})	b_{Ag} (10^{-8} m^2 V^{-1} s^{-1})
	523	0	0.768[a]	38.39[a]	3.06[a]	–
1		0.100	0.778	38.92	3.10 ± 0.00	3.48 ± 0.01
2		0.302	0.791	39.95	3.15 ± 0.01	3.56 ± 0.01
3		0.510	0.801	40.90	3.16 ± 0.01	3.63 ± 0.01
4		0.700	0.815	41.85	3.19 ± 0.03	3.68 ± 0.01
5		0.901	0.822	42.76	3.09 ± 0.10	3.70 ± 0.01
		1	0.830	43.25	–	3.72
	543	0	0.882	38.65	3.53	–
6		0.098	0.888	39.19	3.57 ± 0.00	3.98 ± 0.03
7		0.302	0.896	40.19	3.60 ± 0.01	4.03 ± 0.01
8		0.494	0.898	41.15	3.60 ± 0.02	4.06 ± 0.02
9		0.696	0.909	42.11	3.61 ± 0.03	4.12 ± 0.01
10		0.900	0.911	43.01	3.52 ± 0.09	4.12 ± 0.01
		1	0.918	43.49	–	4.14
	563	0	0.996	38.91	4.02	–
11		0.099	0.997	39.44	4.03 ± 0.00	4.44 ± 0.02
12		0.304	0.999	40.45	4.04 ± 0.01	4.54 ± 0.01
13		0.514	0.995	41.40	4.01 ± 0.01	4.53 ± 0.01
14		0.704	1.000	42.37	3.99 ± 0.05	4.56 ± 0.02
15		0.899	1.000	43.27	3.81 ± 0.16	4.56 ± 0.02
		1	1.003	43.74	–	4.55
	583	0	1.110	39.17	4.51	–
16		0.101	1.107	39.68	4.50 ± 0.00	5.07 ± 0.03
17		0.300	1.100	40.70	4.48 ± 0.01	5.02 ± 0.01
18		0.523	1.093	41.66	4.44 ± 0.01	5.00 ± 0.01
19		0.705	1.087	42.61	4.35 ± 0.03	4.99 ± 0.01
20		0.897	1.082	43.51	4.33 ± 0.16	4.94 ± 0.02
		1	1.085	43.99	–	4.95
	603	0	1.223	39.42	5.00	–
21		0.097	1.213	39.92	4.96 ± 0.01	5.34 ± 0.06
22		0.298	1.200	40.97	4.94 ± 0.01	5.46 ± 0.03
23		0.513	1.187	41.93	4.86 ± 0.01	5.45 ± 0.01
24		0.697	1.174	42.87	4.77 ± 0.03	5.41 ± 0.01
25		0.900	1.163	43.75	4.64 ± 0.20	5.34 ± 0.02
		1	1.164	44.24	–	5.34

[a] The values under the melting point are the ones extrapolated with respect to temperature.

Table 4. Internal mobilities b_K and b_{Ag}. See also the legend of Table 3.

Exp. no.	T (K)	x_{Ag}	$\varkappa$ (10^2 S m^{-1})	V (10^{-6} m^3 mol^{-1})	b_{Li} (10^{-8} m^2 V^{-1} s^{-1})	b_{Ag} (10^{-8} m^2 V^{-1} s^{-1})
	543	0	0.409[a]	52.44[a]	2.22[a]	–
101		0.503	0.634	48.25	2.82 ± 0.01	3.52 ± 0.01
102		0.711	0.750	46.39	3.02 ± 0.01	3.86 ± 0.00
103		0.882	0.856	44.52	3.13 ± 0.01	4.04 ± 0.00
		1	0.918	43.49	–	4.14
	583	0	0.535	53.32	2.96[a]	–
104		0.305	0.677	50.83	3.37 ± 0.00	4.02 ± 0.01
105		0.496	0.780	48.99	3.61 ± 0.01	4.32 ± 0.01
106		0.700	0.894	47.02	3.80 ± 0.01	4.60 ± 0.00
107		0.899	1.019	45.07	3.99 ± 0.01	4.85 ± 0.00
		1	1.085	43.99	–	4.95
	623	0	0.661	54.24	3.72	–
108		0.116	0.710	53.45	3.89 ± 0.00	4.31 ± 0.03
109		0.292	0.810	51.63	4.14 ± 0.00	4.80 ± 0.01
110		0.505	0.918	49.71	4.38 ± 0.01	5.08 ± 0.01
111		0.703	1.036	47.66	4.53 ± 0.01	5.37 ± 0.00
112		0.900	1.168	45.63	4.63 ± 0.01	5.62 ± 0.00
		1	1.238	44.49	–	5.71

[a] See the legend of Table 3.

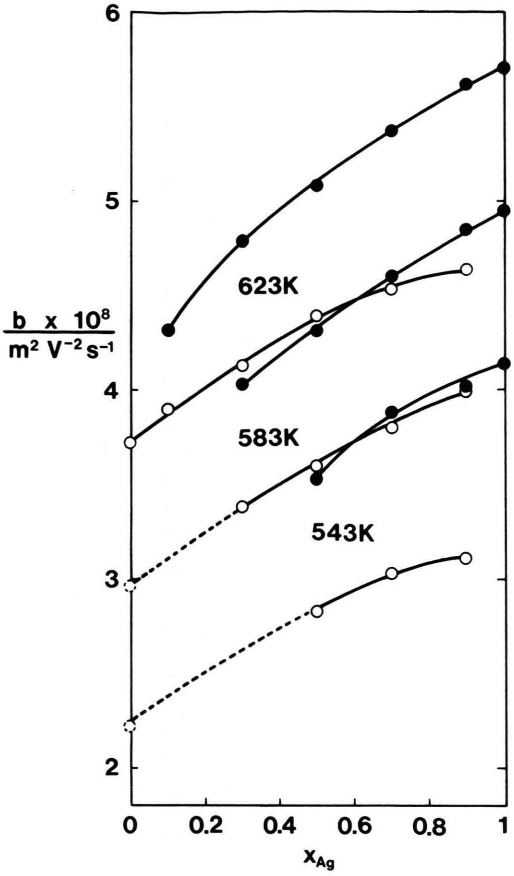

Fig. 3. Internal mobilities in $(K, Ag)NO_3$. ○: K, ●: Ag; ◌: b_K extrapolated with respect to temperature.

Connan [9] measured external transport numbers by the Hittorf method with a silver anode.

The isotherms of the internal mobilities obtained in [5], [6], [8], and [9] are shown in Fig. 4, the internal mobilities in [9] being calculated from their external ones. b_{Ag} is always greater than b_{Li} in all the measurements except in [8], in which a crossing point appears for the isotherms.

For the system $(K, Ag)NO_3$, four original mobility ratio measurements are listed in Table 6. In [10] a silver anode was used. The calculated internal mobility isotherms are shown in Fig. 5. b_{Ag} was greater than b_k in all the measurements except in [12] where a crossing point was observed.

The inherent superiority of the Klemm method to the Hittorf one in this kind of measurements has already been discussed [1]. Here, the errors involved in the EMF method are discussed by using equations

Table 5. A list of the measurements of the mobility ratio in $(Li, Ag)NO_3$.

Author	Ref.	Year	Method	T/K	Agreement
Kawamura	[4]	1968	Hittorf	573	poor[a]
Kawamura & M. Okada	[5]	1971	Hittorf	573	fair
M. Okada & Kawamura	[6]	1971	EMF (A)	573	good
Richter & Armkreutz	[8]	1972	EMF (B)	513–573	poor
Connan	[9]	1973	Hittorf	573	good
I. Okada & Ichioka	This work	1992	Klemm	523–603	–

[a] In [5], the author admits mistakes in the chemical analyses.

Table 6. A list of the measurements of the mobility ratio in $(K, Ag)NO_3$.

Author	Ref.	Year	Method	T/K	Agreement
Duke & Owens	[10]	1958	Hittorf	623	good
M. Okada & Kawamura	[11]	1970	EMF (A)	573	good
Connan	[9]	1973	Hittorf	573	fair
Richter et al.	[12]	1978	EMF (B)	503–623	poor
I. Okada & Ichioka	This work	1992	Klemm	543–623	–

derived in [7]:

$$d\phi_A/d\mu_{Ag} = x_{Ag}\,\varepsilon_{Alk\,Ag}/F, \tag{3}$$

and

$$d\phi_B/d\mu_{Ag} = (1 + x_{Ag}\,\varepsilon_{Alk\,Ag})/F, \tag{4}$$

where F is the Faraday constant, ϕ_A and ϕ_B are the EMF's of cells of types A and B, respectively, and $d\mu_{Ag} = RT\,d\ln a_{Ag}$, where μ_{Ag} is the chemical potential and a_{Ag} the activity of $AgNO_3$ in the mixture. ϕ_A is called diffusion potential.

In order to estimate the error made in [6] when measuring ε in $(Li, Ag)NO_3$ with cells of type A, we rewrite (3) in the form

$$\varepsilon_{Alk\,Ag\,k} = Z_A/x_{Ag} \tag{5}$$

with $Z_A = -d\phi_A/dE$ and $E = -(RT/F)\ln a_{Ag}$. ϕ_A has been determined in [6] to be

$$\phi_A = -A\,10^{-BE} + C \tag{6}$$

with $A = 6.10$ mV, $B = 0.0148\ \mathrm{mV}^{-1}$, and $C = 6.00$ mV. Consequently

$$Z_A = -AB\,(\ln 10)\,10^{-BE}. \tag{7}$$

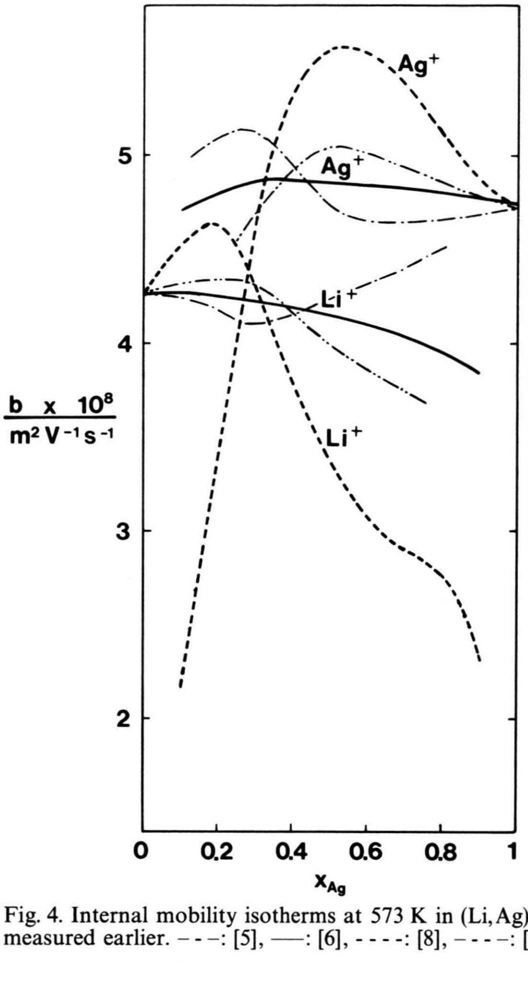

Fig. 4. Internal mobility isotherms at 573 K in (Li, Ag)NO$_3$ measured earlier. – – –: [5], ——: [6], - - - -: [8], – - – -: [9].

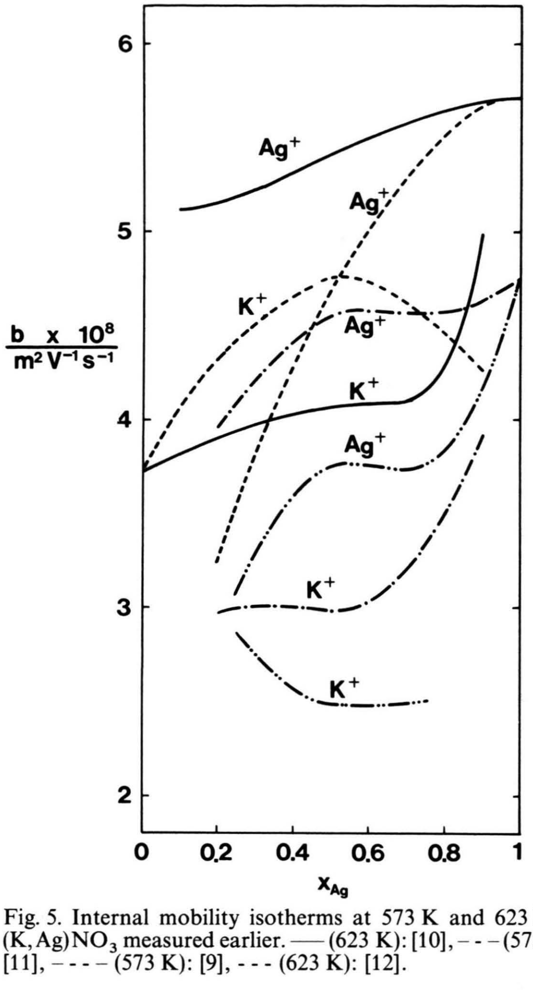

Fig. 5. Internal mobility isotherms at 573 K and 623 K in (K, Ag)NO$_3$ measured earlier. —— (623 K): [10], – – – (573 K): [11], – - – - (573 K): [9], - - - (623 K): [12].

The error of Z_A is

$$\sigma_{Z_A} = \sqrt{(\delta Z_A/\delta E)^2\,\sigma_E^2 + (\delta Z_A/\delta\phi_A)^2\,\sigma_{\phi_A}^2}$$
$$= B\ln 10\sqrt{Z_A^2\,\sigma_E^2 + \sigma_{\phi_A}^2} \approx |B(\ln 10)\,\sigma_{\phi_A}|. \qquad (8)$$

It is assumed from [6] that $\sigma_{\phi_A} \approx 0.3$ mV. Therefore one obtains

$$\varepsilon_{\mathrm{Li\,Ag}}(x_{\mathrm{Ag}} = 0.1) = -0.095 \pm 0.1,$$
$$\varepsilon_{\mathrm{Li\,Ag}}(x_{\mathrm{Ag}} = 0.9) = -0.195 \pm 0.011. \qquad (9)$$

Thus it could not be clarified with this method whether at low x_{Ag} Li$^+$ or Ag$^+$ is more mobile.

As seen from a comparison of (3) and (4), $\mathrm{d}\phi_B/\mathrm{d}\mu_{\mathrm{Ag}}$ is larger than $\mathrm{d}\phi_A/\mathrm{d}\mu_{\mathrm{Ag}}$, even much larger if $x_{\mathrm{Ag}}\,\varepsilon_{\mathrm{Alk\,Ag}}$ is small. Therefore, in order to measure $x_{\mathrm{Ag}}\,\varepsilon_{\mathrm{AlkAg}}$ it is preferable to use cells of type A instead of type B, since the errors involved when measuring a quantity (in this case $\mathrm{d}\phi_A/\mathrm{d}\mu_{\mathrm{Ag}}$ or $\mathrm{d}\phi_B/\mathrm{d}\phi_{\mathrm{Ag}}$) can be assumed to be proportional to the magnitude of this quantity.

Tables 1 and 2 reveal that errors involved in the Klemm method are much lower, particularly at low x_{Ag}, than those in the EMF methods. Thus, it is not surprising that internal mobilities measured by the EMF method deviate from those measured by the Klemm method, particularly at low x_{Ag}.

Further, it should be noted that an apparently small error in the internal transport number of a binary system becomes an enlarged error in ε and hence in the internal mobility particularly at low concentrations. From

$$\varepsilon_{12} = (t_1 - x_1)/x_1 x_2 = (x_2 - t_2)/x_1 x_2, \qquad (10)$$

it follows that

$$\sigma_{\varepsilon_{12}} = \sigma_t/x_1 x_2, \qquad (11)$$

where t is the internal transport number and subscripts 1 and 2 refer to cations 1 and 2 in an additive binary system. An error of $\sigma_t = 0.01$, for example, which often occurs with data measured by the Hittorf and EMF methods, corresponds to an error of as much as $\sigma_{\varepsilon_{12}} = 0.11$ at x_1 or $x_2 = 0.1$.

Thus, the EMF method is inferior to the Klemm method for the determination of ε_{12} for the following reasons:

1. Activities have to be measured independently which inevitably involves considerable errors.
2. Emf's are, in general, more sensitive to impurities than mobilities.
3. At low concentration of a given ion, the error in ε is enlarged. Further, when cells of type B are used, only the small deviation of $F\,d\phi_B/d\mu_2$ from unity yields the information about ε_{12}.
4. The EMF methods can be applied only for additive binary systems and not even for additive ternary systems.

Discussion

It is not known how the mobilities of pure molten salts depend on the interactions of the ions. Why, for instance, is $(b_{+-})_{LiCl} > (b_{+-})_{AgCl}$ but $(b_{+-})_{LiNO_3} < (b_{+-})_{AgNO_3}$? In the discussion of the mobilities of the (Alk, Ag)NO_3 systems we shall therefore take the mobilities of the respective pure salts as given without explanation and discuss the observed dependencies of the isotherms on concentration and temperature in terms of the ion-coion interaction and the two ion-counterion interactions.

To start with (K, Ag)NO_3 (Fig. 3), in the corresponding pure salts the smaller cation (Ag^+, $r = 115$ pm [14]) is more mobile than the larger cation (K^+, $r = 138$ pm [14]). In the mixtures, the ion-coion interaction accelerates the K^+ ion and retards the Ag^+ ions in their migration towards the cathode. Therefore the mobilities of both ions tend to increase with increasing Ag^+-concentration. The same tendency results from the ion-counterion interactions: Ag^+, being smaller than K^+, binds NO_3^- more tightly than K^+ does. If in the mixture some of the K^+-ions are replaced by Ag^+ ions, fewer NO_3^- ions become available for ion-counterion associations, which results in an increase of the mobilities of both cations. Also, on increasing the Ag^+ concentration the decrease of the association of Ag^+ with NO_3^- is greater than that of K^+ with NO_3^- [15]; therefore the increase of the mobility of Ag^+ should be steeper than that of K^+. Figure 3 confirms these predictions: There is a substantial increase of the mobilities of both cations with increasing Ag^+ concentration, and the increase is steeper for Ag^+ than for K^+. The increase of K^+ is somewhat smaller than expected from the empirical relation

$$b_K = (A/(V - V_0)) \exp(-E/RT) \qquad (12)$$

with the coefficients A, V_0 and E obtained from the system (K, Na)NO_3 [16]. Since the molar volumes V of (K, Ag)NO_3 and (K, Na)NO_3 are approximately equal, one would expect equal values of b_K for the two systems. Instead, e.g. for $x_K = 0.2$ at 623 K one has $b_K = 4.5 \cdot 10^{-8}\,m^2\,V^{-2}\,s^{-1}$ for (K, Ag)NO_3 and $b_K = 5.0 \cdot 10^{-8}\,m^2\,V^{-2}\,s^{-1}$ for (K, Na)NO_3.

In case of the system (Li, Ag)NO_3 (Fig. 1) the situation is different, in the corresponding pure salts the smaller cation (Li^+, $r = 59$ pm (IV) and 76 pm (VI) [14]) being less mobile than the larger cation (Ag^+, $r = 115$ pm [14]). This causes a partial cancellation of the tendencies resulting from the ion-coion and ion-counterion interactions, i.e. the isotherms are flatter than in case of (K, Ag)NO_3. At the low temperature ($T = 523$ K), the effect of the ion-coion interaction dominates, i.e. the mobilities of both ions tend to increase with increasing Ag^+-concentration. At the high temperature ($T = 603$ K), however, the effect of the ion-counterion interactions dominates: Ag^+ binds NO_3^- less tightly than Li^+ does. If some of the Li^+ ions are replaced by Ag^+ ions, more NO_3^- ions become available for ion-counterion associations, which results in a decrease of the mobilities of both cations. With increasing Ag^+ concentration the increase in NO_3^- association with Li^+ ions is greater than that with Ag^+ ions; therefore the decrease of the mobility of the Li^+ ions is steeper than that of the Ag^+ ions [15], as observed. The observed temperature effect conforms with the general tendency that molten salts become more molecular with increasing temperature [7].

It should be mentioned that the profiles of the mobility isotherms in (Li, Ag)NO_3 reasonably resemble those in (Li, Na)NO_3 [17].

For the system (Na, Ag)NO_3, the situation is somewhat complicated. The ionic radius of Ag^+ ($r = 115$ pm [14]) seems to be greater than that of Na^+ ($r = 102$ pm [14]), whereas the molar volume of molten AgX ($X = NO_3^-$, Cl^-, Br^-, and I^-) is appreciably greater than that of molten NaX. One interpretation is that the effective ionic radius in the molten state may differ from that in the solid state. An alternative one is that repulsion between Ag^+ ions may be weaker than that between Na^+ ions. In any case, in the corresponding pure molten nitrates Ag^+ is more mobile than Na^+. One may therefore infer that Na^+ binds the counterions more tightly than Ag^+ does. Then the mobility isotherms in (Na, Ag)NO_3 should be similar to those in (Li, Ag)NO_3, as indeed they are.

We are indebted to Professor A. Klemm for helpful discussions.

The expenses of this work have been defrayed by the Grant-in-Aid for Scientific Research No. 03453046 and the Grant-in-Aid for Scientific Research on Priority Area No. 03231103 from the Ministry of Education, Culture and Science, Japan.

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