Internal Mobilities in the Molten Binary Systems (Tl, K)NO_3 and (Tl, Cs)NO_3

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Z. Naturforsch. **52a,** 441–446 (1997); received March 3, 1996

Ratios of internal cation mobilities in the molten binary systems (Tl, K)NO_3 and (Tl, Cs)NO_3 have been measured by the Klemm method. From these and the data available on the densities and electric conductivities, the internal mobilities b have been calculated. While generally in the mixtures of $TlNO_3$ with alkali nitrates at constant temperature the conductivities and internal mobilities decrease with increasing molar volume, in (Tl, K)NO_3 they decrease with decreasing molar volume. This is explained by the high polarizability of the Tl^+ ions.

Key words: Internal mobility, Klemm method, molten (Tl, K)NO_3, molten (Tl, Cs)NO_3, high polarizability.

Introduction

The internal mobilities in the molten systems (Li, Tl)NO_3, (Na, Tl)NO_3 and (Tl, Rb)NO_3 have been studied in [1], [2] and [1], respectively, using Klemm's countercurrent electromigration method. In the present study the internal mobilities in the systems (Tl, K)NO_3 and (Tl, Cs)NO_3 have been measured by the same method.

One of the main aims of the present work was to understand the internal mobilities of these five systems in terms of the high polarizability of the Tl(I) ion.

Experimental

The experimental procedure was quite similar to that described in [2].

Potassium nitrate and thallous nitrate of reagent grade made by Kanto Chemical Co. and caesium nitrate of the same grade made by Wako Chemical Co. were used.

The amount of K^+ and Tl^+ in the separation tube after electromigration was measured with emission spectrophotometry, and that of Cs^+ with atomic absorption spectrophotometry.

The relative differences in internal mobilities, ε, were determined from the change of the mole fractions toward the anode during electromigration. From

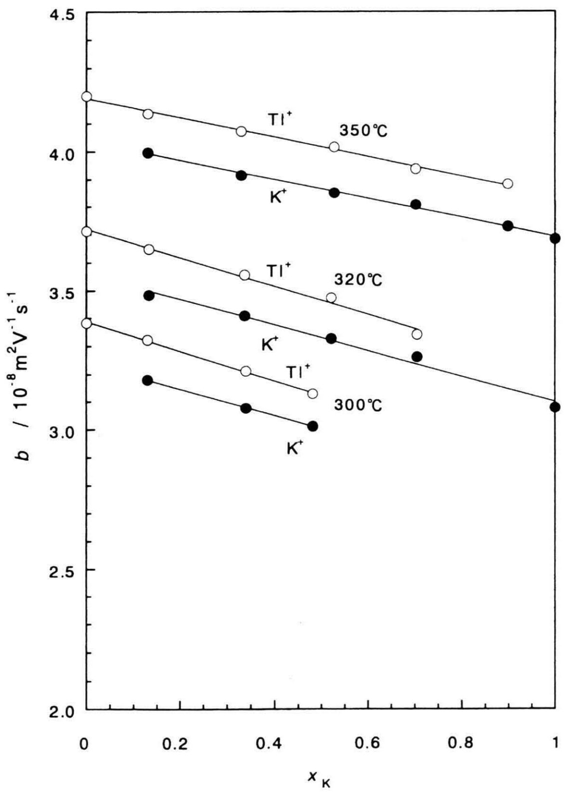

Fig. 1. Internal cation mobilities vs. mole fraction of K^+ in the molten system (Tl, K)NO_3.

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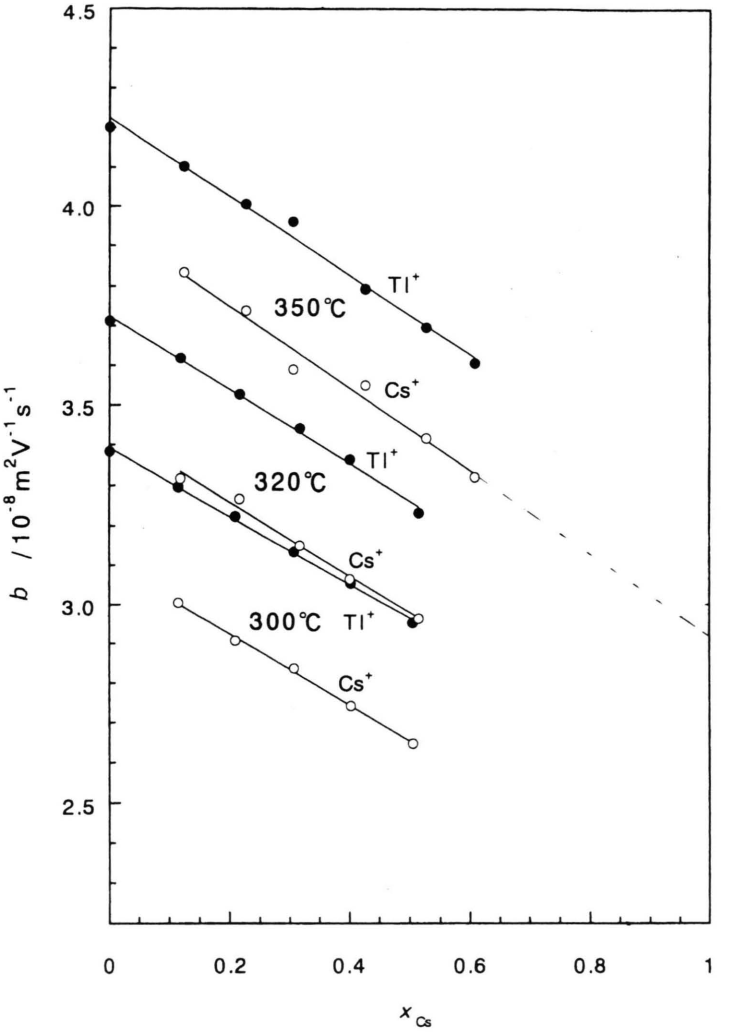

Fig. 2. Internal cation mobilities vs. mole fraction of Cs$^+$ in the molten system (Tl, Cs)NO$_3$.

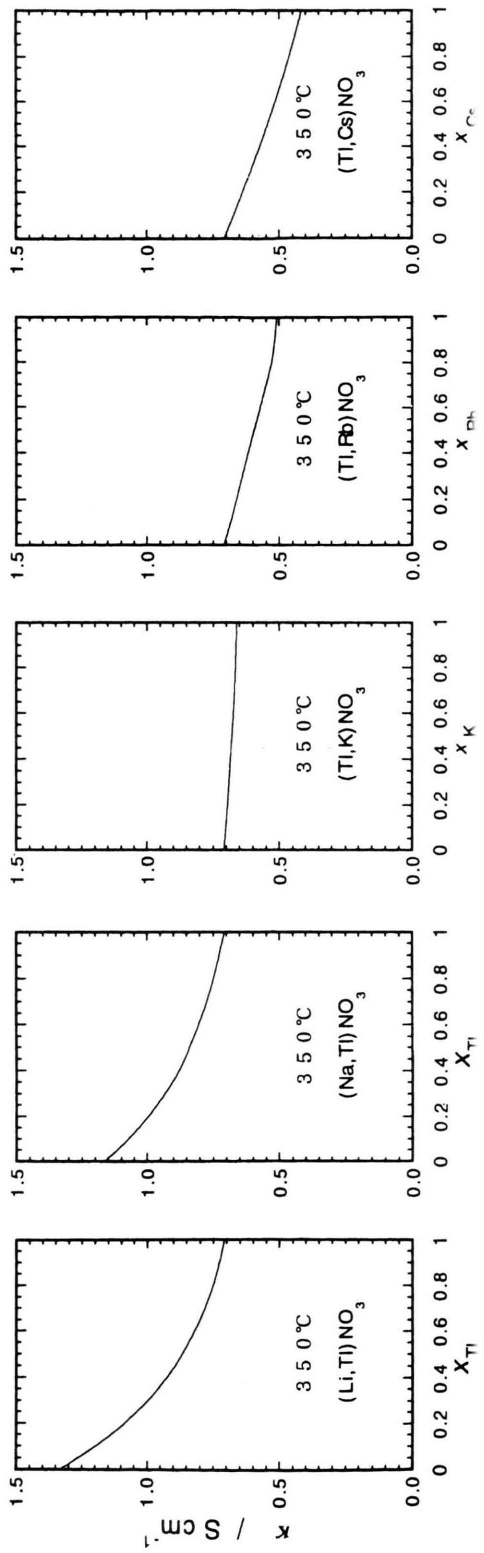

Fig. 3. Conductivities, internal mobilities and molar volumes of five thallium-systems at 350 °C vs. the mole fraction of the salt with the smaller conductivity. (see p. 442–443).

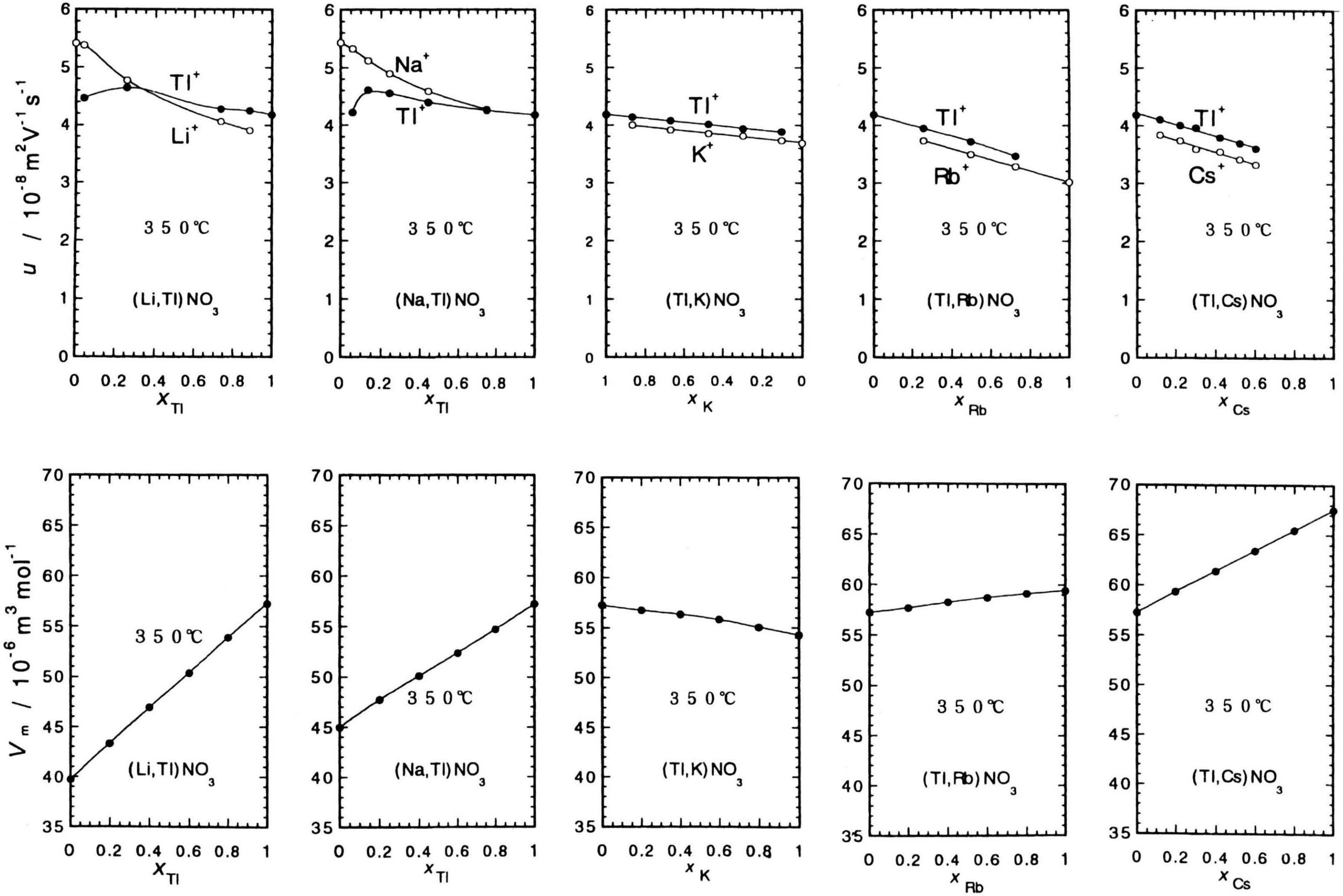
u / 10^-8 m^2 V^-1 s^-1
0
1
2
3
4
5
6
Tl+
Li+
350℃
(Li,Tl)NO3
x_Tl
Na+
Tl+
(Na,Tl)NO3
Tl+
K+
(Tl,K)NO3
x_K
Tl+
Rb+
(Tl,Rb)NO3
x_Rb
Tl+
Cs+
(Tl,Cs)NO3
x_Cs
0
0.2
0.4
0.6
0.8
1
V_m / 10^-6 m^3 mol^-1
35
40
45
50
55
60
65
70

Table 1. Main experimental conditions and internal cation mobilities in the molten system (Tl, K)NO_3. x_K = mole fraction of K, Q = transported electric charge, ε = relative difference in the internal mobilities.

T (°C)	x_K	Q (C)	ε	$\varkappa$ (S m^{-1})	V_m (10^{-6} m^3/mol)	b_{Tl}	b_K
						(10^{-8} m^2 V^{-1} s^{-1})	
300	0			58.13	56.17	3.384	–
	0.130 ± 0.002	1563	−0.0431 ± 0.003	57.13	55.81	3.324 ± 0.001	3.181 ± 0.008
	0.339 ± 0.002	1638	−0.0428 ± 0.001	55.26	55.30	3.213 ± 0.001	3.078 ± 0.003
	0.418 ± 0.007	1642	−0.0381 ± 0.004	54.07	54.85	3.130 ± 0.006	3.013 ± 0.007
320	0			63.31	56.60	3.713	–
	0.133 ± 0.003	1121	−0.0452 ± 0.005	62.26	56.21	3.649 ± 0.002	3.485 ± 0.016
	0.337 ± 0.005	1601	−0.0424 ± 0.004	60.68	55.77	3.558 ± 0.004	3.409 ± 0.009
	0.521 ± 0.004	1708	−0.0434 ± 0.002	59.37	55.23	3.476 ± 0.004	3.328 ± 0.004
	0.705 ± 0.001	1827	−0.0240 ± 0.001	58.18	54.50	3.342 ± 0.004	3.263 ± 0.001
	1					–	3.079
350	0			70.78	57.28	4.201	–
	0.131 ± 0.004	1105	−0.0336 ± 0.005	69.91	56.83	4.137 ± 0.002	3.998 ± 0.019
	0.330 ± 0.003	1604	−0.0387 ± 0.001	68.69	56.49	4.073 ± 0.002	3.917 ± 0.004
	0.527 ± 0.002	1603	−0.0417 ± 0.001	67.67	56.03	4.016 ± 0.003	3.852 ± 0.002
	0.702 ± 0.005	1806	−0.0340 ± 0.004	66.92	55.46	3.939 ± 0.011	3.808 ± 0.004
	0.898 ± 0.002	1997	−0.0406 ± 0.015	66.26	54.53	3.883 ± 0.050	3.730 ± 0.005
	1			66.10	54.24	–	3.685

Table 3. Some fundamental properties of alkali metal ions and their nitrate melts.

	$LiNO_3$	$NaNO_3$	KNO_3	$RbNO_3$	$CsNO_3$	$TlNO_3$
Cation						
ionic radius^a (pm)	59(IV)	102(VI)	138(VI)	152(VI)	167(VI)	150(VI)
ionic mass	6.941	22.98	39.09	85.46	132.9	204.3
polarizability^b (10^{-30} m^3)	0.030	0.182	0.844	1.42	2.45	3.50
Salt						
melting point (°C)	261	308	333	316	414	206
molar volume at 350 °C^c (10^{-6} m^3 mol^{-1})	39.64	44.95	54.24	59.34	(67.48)	57.28
conductivity at 350 °C (S m^{-1})	133.56	115.96	66.10	50.89	(41.46)	70.78

[a] Taken from [4]; the coordination numbers are given in Roman in parentheses.
[b] Values taken from [5].
[c] Values taken from [3]; the value of $CsNO_3$ below the melting point is an extrapolated one with respect to temperature.

Table 2. Main experimental conditions and internal cation mobilities in the molten system (Tl, Cs)NO_3. x_{Cs} = mole fraction of Cs^+.

T (°C)	x_{Cs}	Q (C)	ε	$\varkappa$ (S m^{-1})	V_m (10^{-6} m^3/mol)	b_{Tl}	b_{Cs}
						(10^{-8} m^2 V^{-1} s^{-1})	
300	0			56.17	56.17	3.384	–
	0.115 ± 0.003	1704	0.089 ± 0.008	55.02	57.20	3.296 ± 0.023	3.005 ± 0.003
	0.209 ± 0.000	1611	0.099 ± 0.001	52.48	58.05	3.224 ± 0.003	2.908 ± 0.001
	0.307 ± 0.003	1435	0.097 ± 0.003	49.83	58.93	3.135 ± 0.006	2.838 ± 0.003
	0.402 ± 0.003	1858	0.106 ± 0.002	47.26	59.79	3.055 ± 0.003	2.742 ± 0.003
	0.505 ± 0.000	1113	0.109 ± 0.002	44.49	60.71	2.954 ± 0.003	2.648 ± 0.003
320	0			63.31	56.60	3.713	–
	0.118 ± 0.002	1692	0.084 ± 0.007	59.93	57.69	3.619 ± 0.023	3.317 ± 0.003
	0.216 ± 0.004	1745	0.074 ± 0.006	57.14	58.60	3.527 ± 0.016	3.267 ± 0.004
	0.317 ± 0.003	1445	0.086 ± 0.003	54.24	59.54	3.441 ± 0.008	3.152 ± 0.003
	0.401 ± 0.000	1903	0.091 ± 0.001	51.89	60.31	3.363 ± 0.003	3.066 ± 0.002
	0.515 ± 0.005	1051	0.086 ± 0.008	48.66	61.37	3.233 ± 0.012	2.965 ± 0.013
350	0			70.78	57.28	4.201	–
	0.876 ± 0.002	1674	0.066 ± 0.004	67.18	58.44	4.103 ± 0.017	3.834 ± 0.002
	0.773 ± 0.002	1730	0.067 ± 0.003	64.05	59.43	4.007 ± 0.010	3.739 ± 0.003
	0.695 ± 0.004	1712	0.096 ± 0.003	61.68	60.18	3.961 ± 0.008	3.590 ± 0.003
	0.574 ± 0.002	1802	0.066 ± 0.001	58.00	61.35	3.793 ± 0.003	3.549 ± 0.002
	0.473 ± 0.004	1090	0.079 ± 0.003	54.94	62.32	3.697 ± 0.005	3.416 ± 0.006
	0.392 ± 0.005	1820	0.083 ± 0.003	52.47	63.10	3.606 ± 0.004	3.320 ± 0.006

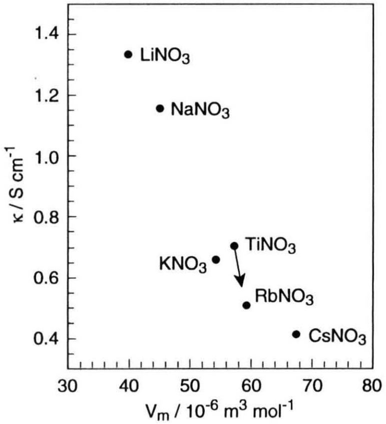

Fig. 4. The conductivity of the alkali nitrates and thallium nitrate vs. their molar volume at 350 °C.

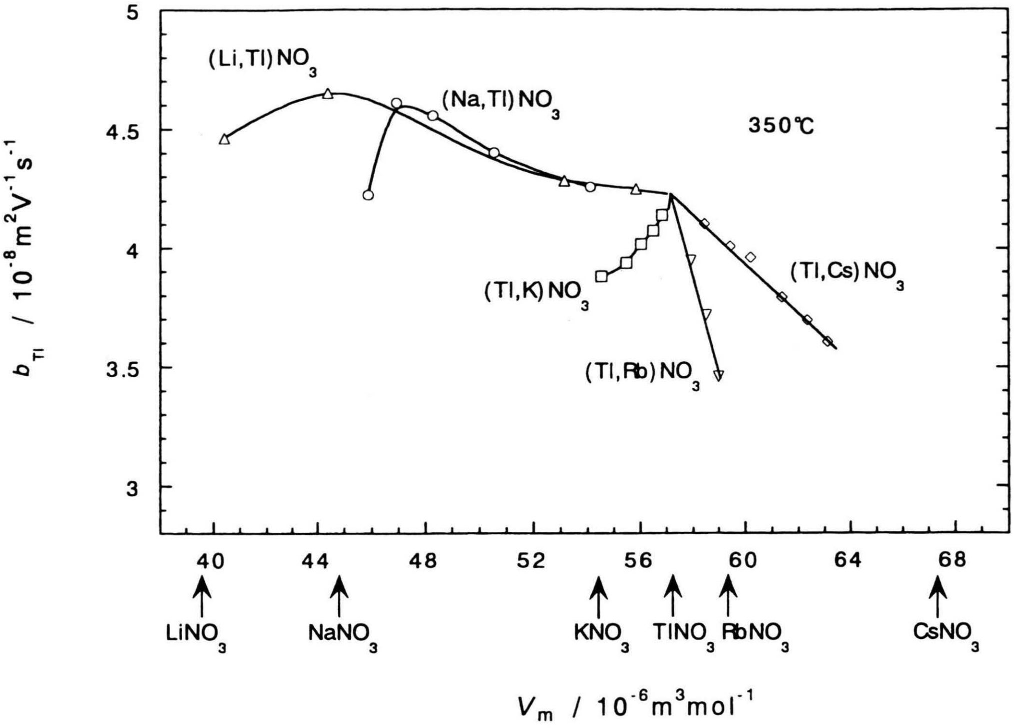

Fig. 5. The mobilities of Tl^+ in binary mixtures of thallium nitrate with the alkali nitrates as a function of the molar volume.

these and the densities and electric conductivities [3], the internal cation mobilities were calculated. The densities of (Tl, Cs)NO_3 are not available and therefore in this case additivity of the molar volumes was assumed.

Results and Discussion

The main experimental conditions and the results for (Tl, K)NO_3 and (Tl, Cs)NO_3 are given in Tables 1 and 2, respectively. Some properties of the cations and the salts involved in this paper are collected in Table 3. The obtained isotherms of the internal mobilities of (Tl, K)NO_3 and (Tl, Cs)NO_3 are presented in Figs. 1 and 2, respectively.

Figure 3 shows the conductivity-, mobility- and molar volume-isotherms of the five $TlNO_3$ systems at 350 °C. It is seen that for the system (Tl, K)NO_3 the change with concentration of the conductivity and the mobilities parallels that of the molar volume, while this is not the case for the other four systems.

This is due to the high polarizability of the thallium ions (cf. Table 3). The polarizability causes a "softening" of the melt and thereby an increase of the mobility of an ion and a decrease of the molar volume of the melt containing the ion, whereby the former is large than the latter.

In Fig. 4 the conductivities vs. the molar volumes of the six salts involved are plotted. The irregularity for $TlNO_3$ is again seen. If the polarizability of Tl^+ were reduced from $3.5 \cdot 10^{-30}$ m^3 to $1 \cdot 10^{-30}$ m^3, the position of the $TlNO_3$-point in Fig. 4 would shift approximately as indicated by the arrow in Fig. 4, and the irregularity would disappear.

Among the binary alkali nitrate-mixtures, the mobility b of a selected alkali-ion can be approximated by the formula [6]

$$b = [A/(V_m - V_0)] \exp(-E/RT), \quad (1)$$

where A, V_0 and E are constants. For our binary mixtures of $TlNO_3$ with Alk(NO_3), the relation (1) does not hold if Tl^+ is the selected ion (cf. Figure 5).

The agreement with (1) would improve if the polarization of Tl^+ could be reduced. Then all points in Fig. 5 would be shifted similarly as in Fig. 4 the point for $TlNO_3$, and the shift would be largest for the mixtures with high $TlNO_3$-content.

We are indebted to Professor A. Klemm for his valuable suggestion. The present work is financially supported by the Ministry of Education, Science and Culture for Scientific Research (No. 07236103 and No. 03453046).

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