Internal Cation Mobilities in the Molten Binary System (Ag, Tl)NO_3

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Z. Naturforsch. **51a,** 197–199 (1996); received November 27, 1995

Internal mobility ratios in the molten binary system (Ag, Tl)NO_3 have been measured by Klemm's countercurrent electromigration method. In the usual way the internal cation mobilities b have been calculated from these data and those available on the densities and conductivities. In the investigated region of temperature and composition b_{Ag} is greater than b_{Tl}.

Introduction

Papers on the internal cation mobilities in molten (Ag, M)MO_3 and (Tl, M)NO_3 (M = alkali metal ion), as measured by Klemm's countercurrent electromigration method, are listed in Table 1. The system (Ag, Tl)NO_3 studied in the present paper is interesting when compared with the aforementioned systems. The melting points of the eutectic mixtures ($x_{Ag} = 0.486$ and 0.515) are at 81 °C [7], and also the melting points of $AgNO_3$ (212 °C) and $TlNO_3$ (206 °C) are considerably lower than those of the alkali nitrates.

Table 1. Molten binary systems (Ag, M)NO_3 and (Tl, M)NO_3 whose internal cation mobility ratios have so far been studied by Klemm's method.

	M				
	Li^+	Na^+	K^+	Rb^+	Cs^+
Ag^+	[1]	[2]	[1]	[3]	[3]
Tl^+	[4]	[5]	[6]	[4]	[6]

Experimental

The chemicals $AgNO_3$ and $TlNO_3$ of reagent grade, made by Wako Chem. Co. Ltd. and Misawa Chem. Co. Ltd., Japan, respectively, were used without further purification. These salts were vacuum-dried at 180 °C for 48 hr and mixed at chosen ratios by weighing.

For electromigrations above 220 °C, the cell was of the type described in [8]. Molten NH_4NO_3 was used as catholyte, and the large vessel in which the separation tube was set contained the eutectic mixture of (Li, Na, K)NO_3 (30, 17 and 53 mol%; mp.: 120 °C [7]).

For electromigrations below 170 °C a cell of the type shown in [9] was employed, which contained the eutectic mixture of (Li, NH_4)NO_3 (25.3 and 74.7 mol%; mp.: 120 °C [7]) in the large vessel.

A separation tube of Vycor of 4 mm inner diameter was filled with alumina powder (150–180 µm). The temperature of the separation tube was kept constant within ± 2 °C by a controller. After electromigration at 90 mA for a few hours the separation tube was taken out, cleaned on the outside and cut into pieces of 6–7 mm length. Each fraction was dissolved in dilute nitric acid for several hours. The content of Ag and Tl atoms was determined by atomic absorption spectrophotometry and flame spectrophotometry, respectively.

The temperature was measured by an Alumel-Chromel thermocouple, which was located in the eutectic mixture at a distance of about 1.5 cm from the part of the separation tube where the initial concentration did not change. The temperature difference between the thermocouple and the inside of the separation tube was estimated according to [10] to be about 1 °C.

Results

The relative difference in the internal mobilities b_{13} and b_{23} (1 = Ag, 2 = Tl, 3 = NO_3), defined by

$$\varepsilon = (b_{13} - b_{23})/b_c , \tag{1}$$

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Table 2. Experimental conditions and ε in the molten system (Ag, Tl)NO_3. Q is the transported charge.

T/°C	x_{Tl}	Q/C	ε
120	0.398±0.001	982	0.266±0.008
	0.493±0.002	927	0.269±0.003
	0.571±0.003	1003	0.220±0.002
140	0.391±0.002	959	0.332±0.004
	0.498±0.001	947	0.338±0.003
	0.579±0.001	986	0.247±0.001
170	0.278±0.004	998	0.310±0.009
	0.492±0.002	1084	0.319±0.004
	0.693±0.002	921	0.328±0.004
220	0.050±0.000	1030	0.270±0.003
	0.105±0.001	1075	0.223±0.008
	0.291±0.001	1040	0.214±0.004
	0.479±0.000	1051	0.283±0.003
	0.698±0.002	1046	0.286±0.004
	0.919±0.003	1099	0.181±0.005
270	0.046±0.001	1117	0.302±0.015
	0.098±0.001	1037	0.246±0.010
	0.300±0.001	1036	0.254±0.004
	0.488±0.004	1091	0.251±0.005
	0.691±0.002	1097	0.247±0.002
	0.901±0.002	1094	0.195±0.010
320	0.047±0.001	1051	0.247±0.010
	0.096±0.002	1046	0.258±0.014
	0.302±0.001	1065	0.217±0.002
	0.496±0.002	1011	0.227±0.003
	0.699±0.001	1022	0.225±0.003
	0.888±0.004	1020	0.095±0.006
350	0.047±0.000	1025	0.238±0.007
	0.092±0.001	1060	0.237±0.010
	0.300±0.000	1061	0.204±0.002
	0.475±0.003	1062	0.203±0.004
	0.697±0.002	1045	0.208±0.004
	0.888±0.003	1045	0.116±0.006

Table 3. Internal mobilities of Ag^+ and Tl^+ in the molten system (Ag, Tl)NO_3.

T/°C	x_{Tl}	κ 10^2 S m^{-1}	V_m 10^{-6} m^3 mol^{-1}	b_{Ag} 10^{-8} m^2 $V^{-1}s^{-1}$	b_{Tl} 10^{-8} m^2 $V^{-1}s^{-1}$
120	0.398	0.1722	45.84	0.905±0.002	0.687±0.004
	0.493	0.1634	46.89	0.900±0.001	0.685±0.001
	0.571	0.1570	47.75	0.875±0.001	0.704±0.000
140	0.391	0.2457	46.05	1.325±0.002	0.935±0.003
	0.498	0.2312	47.24	1.323±0.001	0.938±0.001
	0.579	0.2213	48.15	1.263±0.001	0.989±0.000
170	0.278	0.3831	45.21	1.951±0.005	1.394±0.013
	0.492	0.3350	47.64	1.915±0.003	1.387±0.003
	0.693	0.2968	49.96	1.887±0.005	1.383±0.002
220	0.000	0.6902	42.85	3.065	–
	0.050	0.6671	43.37	3.040±0.000	2.228±0.010
	0.105	0.6445	43.96	3.006±0.002	2.350±0.022
	0.291	0.5732	46.06	2.908±0.003	2.320±0.007
	0.479	0.5097	48.27	2.898±0.004	2.174±0.004
	0.689	0.4468	50.90	2.829±0.007	2.155±0.003
	0.919	0.3955	53.53	2.561±0.011	2.163±0.001
	1.000	0.3778	54.45	–	2.132
270	0.000	0.9168	43.47	4.130	–
	0.046	0.8876	43.96	4.102±0.003	2.878±0.060
	0.098	0.8590	44.54	4.063±0.004	3.086±0.035
	0.300	0.7565	46.89	3.958±0.004	3.023±0.010
	0.488	0.6735	49.19	3.856±0.009	2.991±0.009
	0.691	0.5976	51.71	3.751±0.006	2.959±0.002
	0.901	0.5341	54.30	3.536±0.027	2.949±0.003
	1.000	0.5072	55.50	–	2.917
320	0.000	1.1242	44.11	5.139	–
	0.047	1.0910	44.63	5.107±0.002	3.858±0.051
	0.096	1.0595	45.19	5.088±0.007	3.803±0.065
	0.302	0.9360	47.68	4.931±0.003	3.925±0.008
	0.496	0.8343	50.14	4.826±0.007	3.839±0.007
	0.699	0.7428	52.76	4.704±0.022	3.787±0.003
	0.888	0.6715	55.19	4.165±0.014	3.800±0.003
	1.000	0.6331	56.60	–	3.713
350	0.000	1.2375	44.50	5.707	–
	0.047	1.2059	45.03	5.692±0.002	4.350±0.042
	0.092	1.1754	45.56	5.673±0.005	4.355±0.052
	0.300	1.0440	48.12	5.528±0.004	4.463±0.009
	0.475	0.9450	50.38	5.413±0.011	4.408±0.012
	0.697	0.8339	53.32	5.281±0.014	4.318±0.006
	0.888	0.7519	55.83	4.800±0.026	4.295±0.003
	1.000	0.7078	57.28	–	4.201

was derived from an equation [11] which is based on the charge and material balances. Here,

$$b_c = x_{13} b_{13} + x_{23} b_{23} = \kappa V_m / F , \tag{2}$$

where x_{13} and x_{23} are the mole fractions of the salts, κ is the conductivity, V_m the molar volume of the mixture, and F the Faraday constant.

The obtained values of ε are given in Table 2 together with the main experimental conditions. The internal cation mobilities b_{13} and b_{23} were calculated from the ε values and the data [12] on the densities and conductivities. The calculated values are given in Table 3, and the corresponding isotherms are shown in Figs. 1a and 1b. Since at low temperatures the liquid range of the concentrations decreases, the region to be covered for the mobility isotherms b decreased as well.

Discussion

It is usual to identify M_1 of a molten binary $(M_1, M_2)X$ (salt mole fractions x_{13} and $x_{23} = 1 - x_{13}$) with the metal which in the pure salt has a greater internal mobility than M_2 in the pure salt ($b_{13}(0) > b_{23}(1)$). For M_1 = Ag, M_2 = Li, Na, K, Rb or Cs, and X = NO_3, $b_{13}(x_{23})$ was found to be greater than $b_{23}(x_{23})$ in the studied range of concentrations and

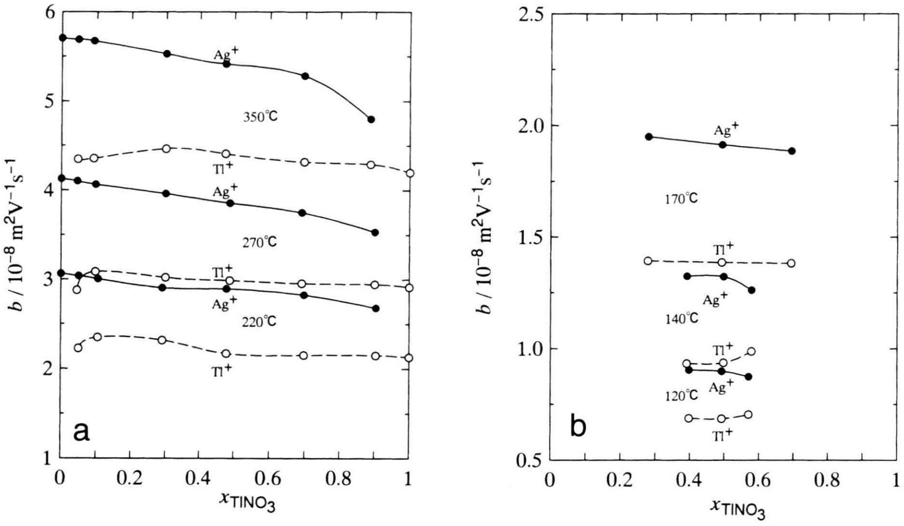

Fig. 1. Isotherms of b_{Ag} and b_{Tl}. (a) 350 °C, 270 °C, and 220 °C, (b) 170 °C, 140 °C, and 120 °C.

temperatures. Figure 1 shows that this is also true for $M_1 = Ag$, $M_2 = Tl$ and $X = NO_3$.

Generally for such binaries, b_{13} and b_{23} decrease with increasing x_{23}, the decrease of b_{13} being steeper than that of b_{23}. Figure 1 shows that for (Ag, Tl)NO_3 this holds generally, but that it does not hold at 120 °C and 140 °C in the range $0.4 < x_{23} < 0.6$, and at 220 °C, 270 °C and 350 °C in the range $0 < x_{23} < 0.2$.

In [6] we will report on the mobilities in (K, Tl)NO_3 and (Cs, Tl)NO_3, so that then all systems listed in Table 1 will have been studied. On this occasion we intend to discuss the observations, including (Ag, Tl)NO_3, in a broader context and in more detail.

Acknowledgements

One of the authors (P. C.) wishes to thank the Rotary Club, Japan for the Yoneyama memorial scholarship.

The expenses of this work have been defrayed by the Grant-in-Aid for Scientific Research on Priority Areas (No. 07236103, Cooperative Phenomena in Complex Liquids) and (B) (No. 07454183) from the Ministry of Education, Science and Culture, Japan.

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