Fused Salt Concentration Cells with Transference. Transport Numbers of Molten (Li,Ag)Cl and Molten Alkali Jodide and Silver Jodide Mixtures

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Dedicated to Professor Rolf Haase on the occasion of his 65th birthday

The transport numbers of the molten systems (Li,Ag)Cl, (Na,Ag)I, (K,Ag)I, and (Rb,Ag)I have been determined by e.m.f. measurements on concentration cells with transference. With the exception of (Na,Ag)I, for these systems the existence of inversion points (the mobility ratio reverses at a certain mixing ratio) is proven within experimental accuracy. For (Na,Ag)I an inversion point might exist at the high AgI concentration side.

In continuation of our studies on alkali halide – silver halide mixtures [1], this paper reports on the transport numbers of the systems (Li,Ag)Cl, (Na,Ag)I, (K,Ag)I, and (Rb,Ag)I over the whole concentration range and temperatures between 800 and 1100 K, as obtained from e.m.f.-measurements on concentration cells of the type

Terminal	Electrode	Melt I	Melt II	Electrode	Terminal
Ag	Ag	MX+AgX (x_I)	MX+AgX (x_II)	Ag	Ag

The measurable e.m.f. Φ_{BB} depends on the liquid junction potential between the melts I and II, and with that on the transport number for the average mole fraction of the two mixtures.

The transport number is given by

$$t_\chi = -x_1 (\Phi'_{BB}/\Phi'_{BC}) , \qquad (1)$$

where t_χ is the transport number of the alkali constituent and x_1 is its mole fraction. Φ_{BB} and Φ_{BC} are the e.m.f.'s of the concentration cell with silver electrodes and of the chemical cell, referred to the standard melt, respectively. The prime indicates differentiation with respect to x_2. If there is an inversion point, $t_\chi - x_1$ changes sign.

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Results

The measured e.m.f. Φ_{BB} was fitted to a linear dependency on temperature at constant x_2:

$$\Phi_{BB} = c + dT . \qquad (2)$$

In Table 1 the coefficients c and d of the investigated systems are listed together with the maximum and mean error of the e.m.f. The transport numbers are evaluated according to (1), where also the derivation of Φ_{BC} comes in.

For (Li,Ag)Cl the Φ_{BC}'s of Salstrom, Kew and Powell [3], and for the iodides the Φ_{BC}'s of Sternberg, Adorian and Galasiu [4, 5] were chosen.

The experimental transport numbers may be fitted by the following polynomial expression depending on the composition and the temperature of the melt:

$$t_{\chi\,\mathrm{fit}} = x_1 + x_1 x_2 [(q_0 + q_1 \ln T) + (r_0 + r_1 \ln T) x_1 + (s_0 + s_1 \ln T) x_1^2] . \qquad (3)$$

The deviations $t_\chi - t_{\chi\,\mathrm{fit}}$ for the systems described here were greater than those for the previous systems [1]. Therefore a fit for the temperature dependence only at a given mole fraction x_2 was tried:

$$t_{\chi e} = a\, e^{-A/T} . \qquad (4)$$

(4) gives very good results. For all four systems the values of the constants $q_0, \ldots, s_1$ of (3) are summed

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Table 1. The constants c and d of (2) for the evaluation of the e.m.f. Φ_{BB} of the systems (Li,Ag)Cl, (Na,Ag)I, (K,Ag)I, and (Rb,Ag)I. Mean deviation $\overline{\delta\Phi_{BB}}$ and maximum deviation $\delta\Phi_{BB}$.

System	Mole fraction x_{AgX}	Constants c / mV	$-d \cdot 10^3$ / mV K^{-1}	Mean dev. $\overline{\delta\Phi_{BB}}$ / mV	Max. dev. $\delta\Phi_{BB}$ / mV
LiCl + AgCl	0.1	82.76	203.03	1.79	3.21
	0.2	66.35	146.45	1.64	2.84
	0.3	49.65	109.26	1.50	2.52
	0.4	37.18	83.51	1.36	2.24
	0.5	26.53	62.57	1.22	1.95
	0.6	18.01	45.63	1.05	1.66
	0.7	11.07	31.07	0.85	1.33
	0.8	5.91	18.87	0.60	0.93
	0.9	2.29	8.65	0.85	1.24
NaI + AgI	0.1	57.97	257.20	1.02	2.03
	0.15	55.91	221.08	0.95	1.89
	0.2	51.58	192.25	0.86	1.72
	0.3	45.96	152.29	0.76	1.50
	0.4	36.73	118.21	0.67	1.29
	0.5	29.73	91.52	0.59	1.12
	0.6	22.79	68.21	0.51	0.94
	0.7	16.69	48.10	0.43	0.77
	0.8	10.48	29.66	0.35	0.59
	0.9	5.30	13.64	0.24	0.39
KI + AgI	0.1	−1.23	266.73	0.98	1.94
	0.15	2.96	230.47	0.90	1.80
	0.2	7.17	203.19	0.82	1.64
	0.3	16.37	163.99	0.72	1.43
	0.4	22.16	131.82	0.63	1.24
	0.5	23.67	102.39	0.55	1.06
	0.6	22.44	75.69	0.47	0.89
	0.7	19.40	52.37	0.39	0.72
	0.8	14.33	32.80	0.31	0.54
	0.9	6.68	13.64	0.21	0.35
RbI + AgI	0.1	−29.20	263.55	1.03	2.07
	0.15	−23.13	226.10	0.96	1.92
	0.2	−16.03	199.72	0.88	1.75
	0.3	− 1.47	161.38	0.78	1.54
	0.4	11.78	132.21	0.69	1.35
	0.5	19.73	104.92	0.61	1.17
	0.6	23.32	80.25	0.53	1.00
	0.7	20.64	55.10	0.44	0.80
	0.8	14.11	31.98	0.35	0.61
	0.9	5.84	12.41	0.24	0.39

Table 2a. Values of the parameters $q_0, \ldots, s_1$ of (3).

	LiCl + AgCl	NaI + AgI	KI + AgI	RbI + AgI
q_0	− 0.9464	− 7.6118	− 18.9157	−7.3570
q_1	0.1435	1.0816	2.6361	0.9901
r_0	14.1992	26.5180	91.5021	−9.1020
r_1	− 2.2378	− 3.5430	− 12.7667	1.5360
s_0	−37.9119	−42.8858	−109.3338	33.5038
s_1	5.8109	5.9274	15.5194	−4.7525

Table 2b. Values of the parameters a and A of (4).

Mole fraction x_{AgCl}	LiCl + AgCl		NaI + AgI	
	a	A	a	A
0.15			1.2373	350.6971
0.2	1.2118	273.7050	1.2497	395.8826
0.3	1.1113	367.7259	1.1498	400.9485
0.4	0.8584	348.2365	1.0108	374.5375
0.5	0.6256	274.4921	0.8173	308.0871
0.6	0.4219	116.7073	0.6636	310.0628
0.7	0.2763	−40.7829	0.5340	392.5678
0.8	0.1741	−98.8809	0.3792	486.7453
0.9	0.0908	27.3667	0.1903	607.6515

Mole fraction x_{AgCl}	KI + AgI		RbI + AgI	
	a	A	a	A
0.15	1.6837	646.7260	1.0443	58.3793
0.2	1.4734	517.8311	0.9736	15.3221
0.3	1.0383	220.4198	0.8508	−31.4282
0.4	0.7568	12.1735	0.7743	20.4530
0.5	0.6045	−19.9349	0.7215	178.0455
0.6	0.5263	135.8386	0.6936	445.4634
0.7	0.4740	478.2547	0.6576	796.8544
0.8	0.4398	950.6701	0.5416	1166.6167
0.9	0.2670	1294.9376	0.2626	1342.9848

Table 3. Measured transport numbers t_α (α = Li, Na, K, Rb), absolute maximum and mean errors, δt_α and $\overline{\delta t_\alpha}$, fits according to (3), $t_{\alpha\,\mathrm{fit}}$, and mobility ratios, u_α/u_β, of the systems (Li,Ag)Cl, (Na,Ag)I, (K,Ag)I, and (Rb,Ag)I at 960 K.

x_{AgCl}	t_α	δt_α	$\overline{\delta t_\alpha}$	$t_{\alpha\,\mathrm{fit}}$	u_α/u_β
			LiCl + AgCl		
0.1	–	–	–	0.954	2.304
0.2	0.913	0.214	0.058	0.861	1.549
0.3	0.760	0.289	0.075	0.741	1.226
0.4	0.600	0.279	0.069	0.613	1.056
0.5	0.471	0.239	0.058	0.488	0.953
0.6	0.374	0.198	0.046	0.374	0.896
0.7	0.288	0.152	0.036	0.272	0.872
0.8	0.193	0.091	0.022	0.182	0.890
0.9	0.088	0.045	0.010	0.095	0.945
			NaI + AgI		
0.1	–	–	–	0.902	1.023
0.15	0.859	0.100	0.026	0.863	1.112
0.2	0.827	0.091	0.024	0.827	1.195
0.3	0.757	0.076	0.020	0.758	1.342
0.4	0.685	0.087	0.023	0.682	1.430
0.5	0.593	0.087	0.023	0.591	1.445
0.6	0.481	0.075	0.020	0.482	1.396
0.7	0.355	0.055	0.015	0.358	1.301
0.8	0.229	0.033	0.009	0.227	1.175
0.9	0.101	0.012	0.003	0.101	1.011
			KI + AgI		
0.1	–	–	–	0.936	1.625
0.15	0.859	0.107	0.026	0.907	1.721
0.2	0.858	0.098	0.024	0.878	1.799
0.3	0.825	0.086	0.022	0.808	1.804
0.4	0.747	0.097	0.025	0.718	1.697
0.5	0.617	0.090	0.024	0.603	1.519
0.6	0.457	0.071	0.019	0.467	1.314
0.7	0.288	0.046	0.013	0.318	1.088
0.8	0.163	0.027	0.008	0.175	0.848
0.9	0.069	0.012	0.004	0.059	0.564
			RbI + AgI		
0.15	0.983	0.110	0.028	–	–
0.2	0.958	0.093	0.023	–	–
0.3	0.879	0.072	0.018	0.885	3.298
0.4	0.758	0.070	0.018	0.749	1.989
0.5	0.599	0.059	0.015	0.595	1.469
0.6	0.436	0.044	0.011	0.438	1.169
0.7	0.286	0.029	0.008	0.290	0.953
0.8	0.161	0.017	0.005	0.163	0.779
0.9	0.065	0.007	0.002	0.064	0.615

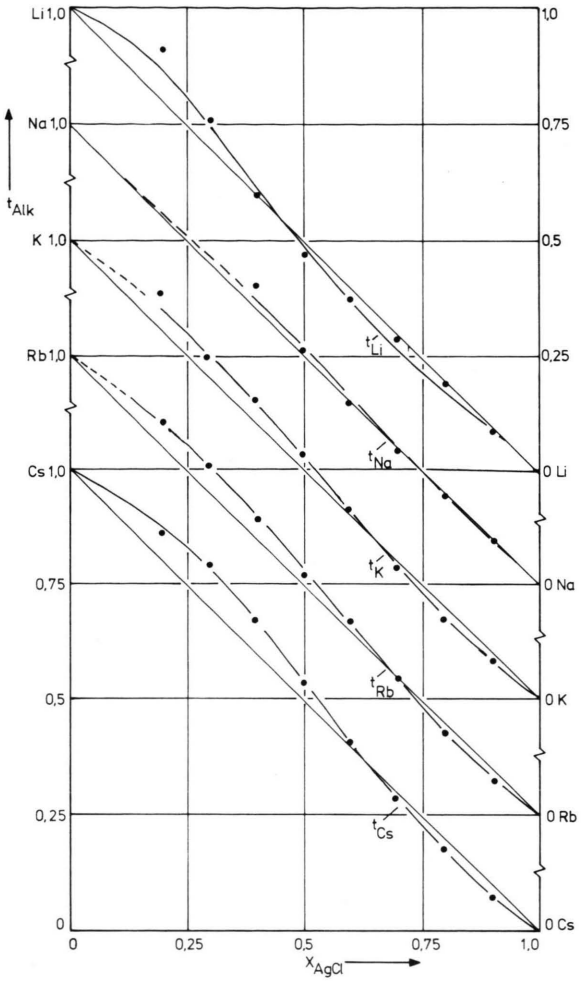

Fig. 1. Transport numbers of the alkali ion constituents in the systems (Li,Ag)Cl, (Na,Ag)Cl, (K,Ag)Cl, (Rb,Ag)Cl, and (Cs,Ag)Cl at 960 K as functions of the mole fraction x_{AgCl}.

up in Table 2a, and those of a and A of (4) in Table 2b. They are at least valid in the temperature range 500–700 °C. Table 3 lists the transport numbers t_α of all four systems at 960 K, calculated according to (1), the absolute maximum errors δt_α, the mean errors $\overline{\delta t_\alpha}$, the $t_{\alpha\,\mathrm{fit}}$, and the mobility ratios u_α/u_β (β = Ag). The errors listed in Table 3 result from the propagation of the mean and maximum errors of the e.m.f. values entering (1).

Figure 1 shows the concentration dependence of the transport numbers of the alkali ion constituents for the chloride systems, those published previously [1] being included, and Fig. 2 the corresponding data for the iodide systems, all at 960 K.

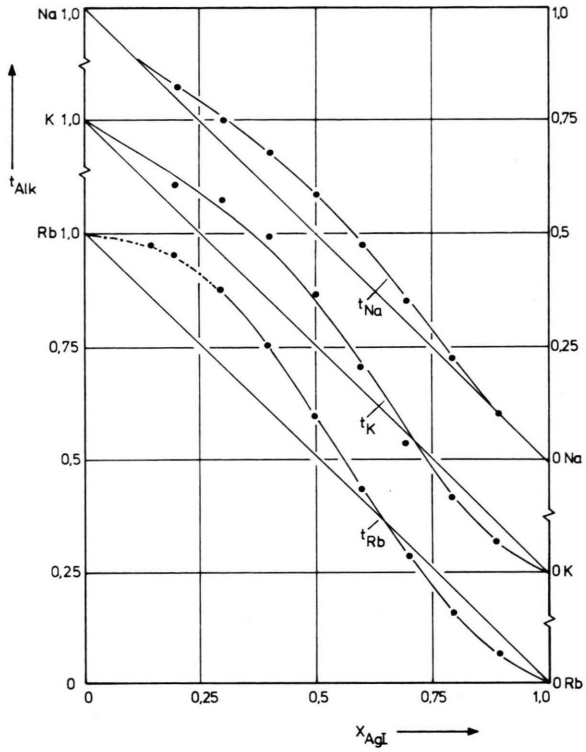

Fig. 2. Transport numbers of the alkali ion constituents in the systems (Na, Ag)I, (K, Ag)I, and (Rb, Ag)I at 960 K as functions of the mole fraction x_{AgI}. The dash-dotted line represents the logical curve between the measured points, as the fit does not give sensible data in this area.

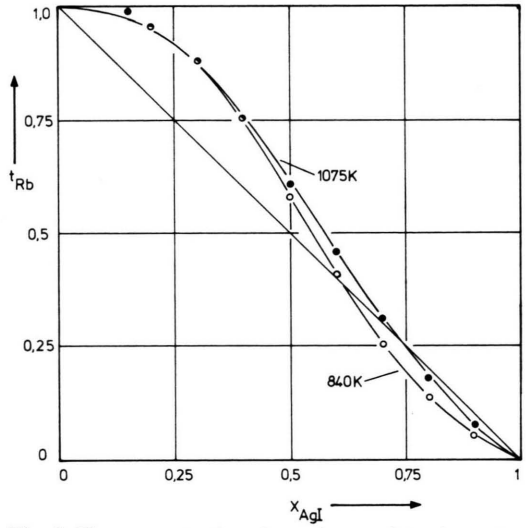

Fig. 3. The concentration dependence of the inversion point at different temperatures of the system (Rb, Ag)I.

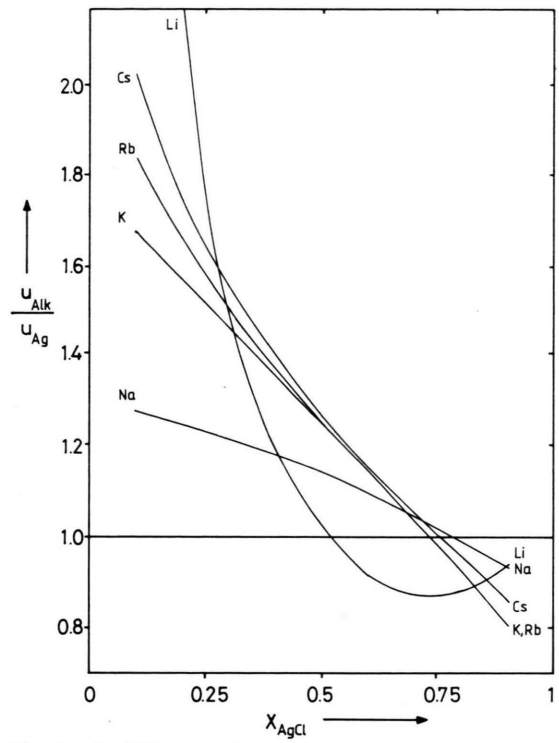

Fig. 4. Mobility ratios of (Li, Ag)Cl, (Na, Ag)Cl, (K, Ag)Cl, (Rb, Ag)Cl, and (Cs, Ag)Cl at 1075 K as functions of the mole fraction x_{AgCl}.

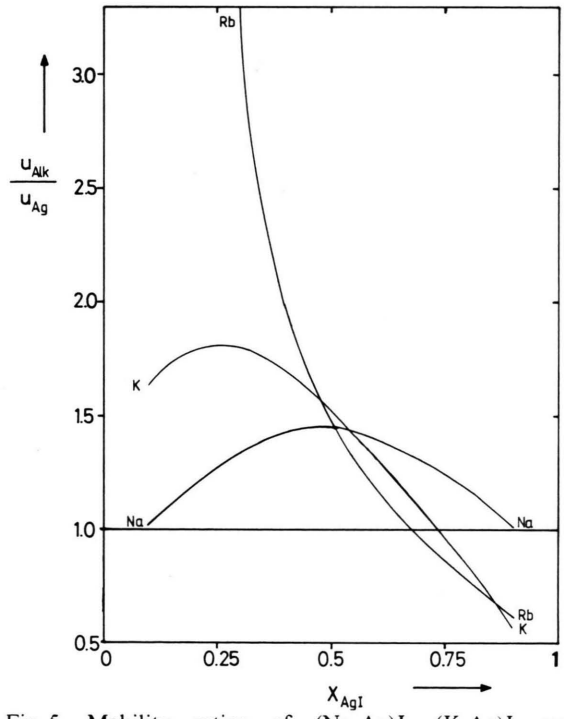

Fig. 5. Mobility ratios of (Na, Ag)I, (K, Ag)I, and (Rb, Ag)I at 960 K as functions of the mole fraction x_{AgCl}.

Discussion

Like the other chloride systems investigated, the system (Li,Ag)Cl and the iodide systems show a non-linearity in the concentration dependence of the transport numbers, and for the systems (Li,Ag)Cl, (K,Ag)I, and (Rb,Ag)I there is an inversion point where the deviation from the linearity $t_\chi = x_1$ changes sign. This deviation is always of the same kind: it is negative when the silver halide concentration is high, and it is positive when it is low. At the inversion point the mobilities of the cations are equal. This point shifts to higher silver halide concentrations with rising temperature.

Only in the system (Na,Ag)I an inversion point could not be proved within the experimental accuracy, similar to the system (Na,Ag)Cl, where only a small effect was visible [1].

In Figs. 4 and 5 the mobility ratios u_χ/u_{Ag} are plotted at 1075 K and 960 K for the chlorides and the iodides, respectively.

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