Electric Conductivities of Binary Molten (K, Ag) Cl, (Cs, Ag) Cl, (K, Ag) Br, (Na, Ag) I, (K, Ag) I, and (Cs, Ag) I Mixtures

H.-P. Boßmann, A. Hildebrandt, and J. Richter
Institut für Physikalische Chemie der RWTH Aachen, Germany

Z. Naturforsch. **41 a**, 1129–1136 (1986); received June 30, 1986

The specific electric conductivities of the binary molten mixtures (K, Ag)Cl, (Cs, Ag)Cl, (K, Ag)Br, (Na, Ag)I, (K, Ag)I, and (Cs, Ag)I are determined as functions of temperature and composition. For 950 K, 1000 K, 1050 K, and 1100 K the equivalent conductivities and the ionic conductivities of the cations with reference to the common anion are evaluated in dependence on the composition.

Introduction

Equivalent conductivities, transport numbers, and diffusion coefficients are suitable material data for the characterization of the transport behaviour of ions in molten salts and are used for the evaluation of the friction coefficients, which can be helpful for a molecular kinetic interpretation of binary fused salts with three ion constituents. The reference system here is the anion constituent, which is common to both components of the system.

In previous papers we have investigated the transport numbers [1–3] and the densities [4, 5] of alkali halide – silver halide melts. In this work the electric conductivities of the systems (K, Ag)Cl, (Cs, Ag)Cl, (K, Ag)Br, (Na, Ag)I, (K, Ag)I, and (Cs, Ag)I are determined with the 4-electrode method in dependence on composition and temperature.

The specific conductivity $\varkappa$ can be evaluated from the cell constant Z of the conductivity cell, described below, and the measured resistance R

$$\varkappa = Z/R\,. \tag{1}$$

The temperature dependence of $\varkappa$ of the systems in this paper can be described by

$$\varkappa = a + bT + cT^2\,. \tag{2}$$

The equivalent conductivity Λ is calculated from $\varkappa$, the density ϱ, and the molar masses M_1 and M_2

$$\Lambda = \frac{\varkappa}{\varrho}\,(x_1 M_1 + x_2 M_2)\,. \tag{3}$$

The concentration dependence of Λ can be fitted quite well by a third order polynomial for the systems investigated in this paper

$$\Lambda = a' + b' x_2 + c' x_2^2 + d' x_2^3\,. \tag{4}$$

The ion conductivities λ_{1+} and λ_{2+} may be calculated from the equivalent conductivity using the transport numbers t_{1+} and t_{2+} of the two cation constituents relative to the common anion constituent ($\lambda_- \equiv 0, t_- \equiv 0$)

$$\lambda_{1+} = \frac{t_{1+}}{x_1}\Lambda\,, \qquad \lambda_{2+} = \frac{t_{2+}}{x_2}\Lambda\,. \tag{5}$$

Here 2+ always represents the silver ion.

Experimental

The measurements were made in a quartz glass cell with an U-shaped capillary between the electrodes (Figure 1). The cell was surrounded by a metal block to improve temperature homogeneity. The diameter of the capillary is about 2 mm leading to a cell constant of about 550 cm^{-1} which is independent of the filling level, provided that the electrodes are completely immersed. Oxygen from the air is excluded by an argon atmosphere [7].

Four 1 cm^2 platinum sheets serve as electrodes. Each of them is connected to a RCL-bridge and a relais-interface, one of them via two platinum wires. This arrangement gives the opportunity to measure the resistance of the cell using the 2-electrode as well as the 4-electrode method and also allows a separate determination of the resistance of the leads which can be subtracted from the total resistance.

Reprint requests to Prof. Dr. J. Richter, Institut f. Physikal. Chemie der RWTH Aachen, Templergraben 59, D-5100 Aachen.

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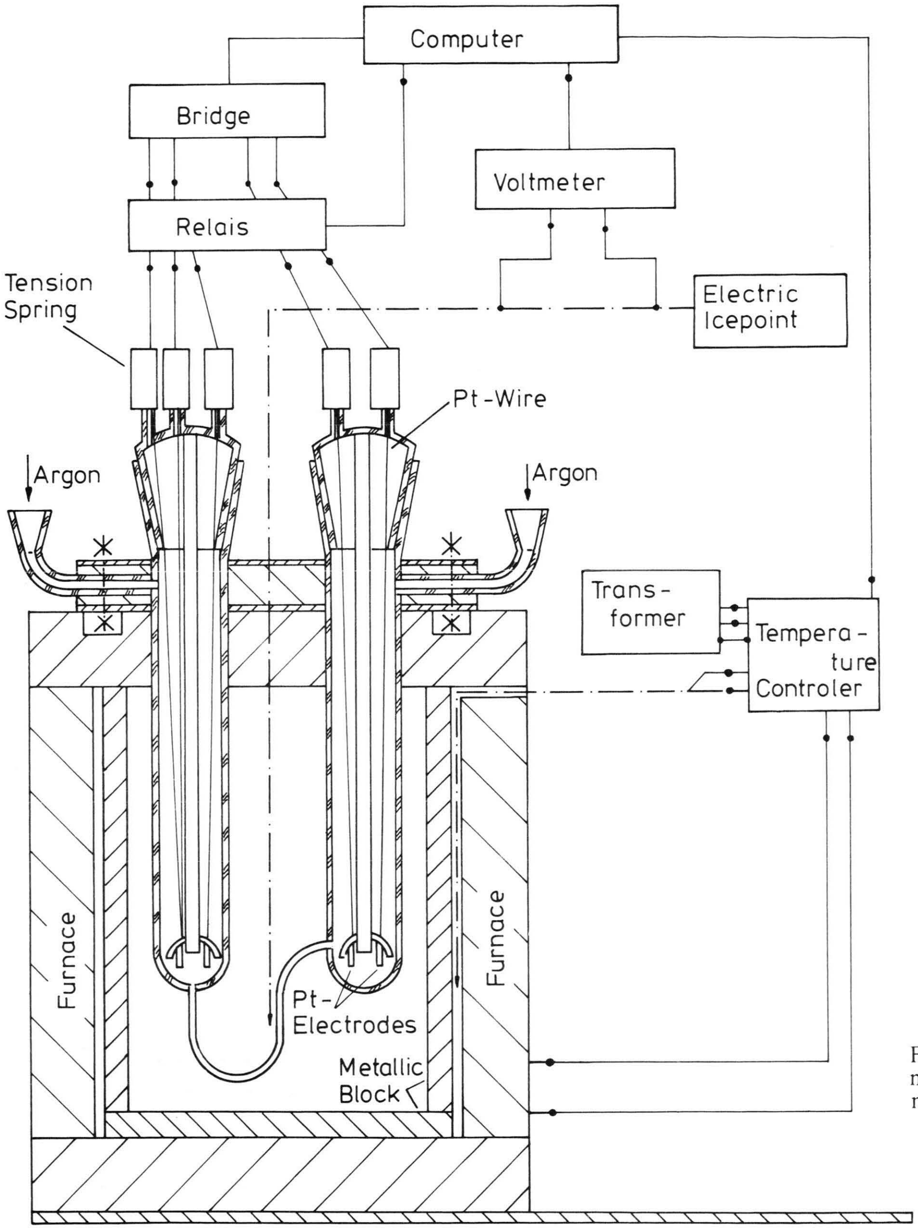

Fig. 1. Conductivity cell, furnace and metal block (schematic).

The 4-electrode method makes possible a quasi currentless impedance measurement. The voltage applied may be varied between 5 mV and 1.275 V and the frequency between 12 Hz and 100 kHz.

The furnace is controlled by a PID-controller, the thermocouples of which measure the temperature in the gap between the metal block and the inner wall of the furnace. The temperature of the melt is measured at the capillary by NiCr-Ni thermocouples. A personal computer is used to control the measuring device and to record the data.

The cell is calibrated with KNO_3 in the temperature range between 615 K and 789 K and with NaCl between 1080 K and 1250 K [8]. The temperature variation of the cell constant is about 0.1% over the total temperature range [9].

Table 1. Constants a, b, and c of (2) for the specific conductivity as a function of the mole fraction of the silver halide in the temperature range from $T_{\min}$ to 1100 K. s_{xy} denotes the standard deviation.

System	x_2	$\frac{T_{\min}}{\mathrm{K}}$	$\frac{a}{S\,\mathrm{cm}^{-1}}$	$\frac{b\,10^3}{S\,\mathrm{cm}^{-1}\,\mathrm{K}^{-1}}$	$\frac{c\,10^6}{S\,\mathrm{cm}^{-1}\,\mathrm{K}^{-2}}$	$\frac{s_{xy}}{\mathrm{cm}^{-1}}$
KCl-AgCl	0.0	1050	-7.1223	14.5160	-5.4124	0.005
	0.1	1020	-4.2093	9.5681	-3.3122	0.020
	0.2	960	-5.0839	11.7440	-4.5533	0.021
	0.3	910	-2.6095	7.3772	-2.5423	0.005
	0.468	810	-3.0267	8.7166	-3.2993	0.030
	0.577	720	-3.0275	9.3238	-3.6907	0.025
	0.7	590	-2.9068	10.0747	-4.2252	0.020
	0.791	630	-2.5322	10.2383	-4.4015	0.023
	0.9	690	-1.8156	9.8418	-4.1006	0.036
	1.0	730	-0.8548	9.0310	-3.5954	0.044
CsCl-AgCl	0.0	920	-2.3881	5.2639	-1.5753	0.000
	0.1	880	-2.4551	5.4513	-1.7050	0.000
	0.2	830	-2.2863	5.2417	-1.6584	0.016
	0.3	760	-2.4853	5.7383	-1.9324	0.000
	0.4	670	-2.5334	6.0870	-2.1822	0.001
	0.5	600	-2.5764	6.5308	-2.4535	0.002
	0.6	580	-2.5876	7.1565	-2.8677	0.006
	0.7	550	-2.4493	7.6527	-3.1582	0.005
	0.8	650	-2.4744	8.8879	-3.8234	0.009
	0.9	700	-1.5019	8.2753	-3.4049	0.004
	1.0	730	-0.8548	9.0310	-3.5954	0.042
KBr-AgBr	0.0	1010	-3.1181	7.0354	-2.3251	0.001
	0.1	980	-1.7361	4.5289	-1.2059	0.001
	0.2	930	-2.5521	6.3342	-2.1847	0.000
	0.3	870	-1.5948	4.6833	-1.4538	0.001
	0.4	810	-1.9861	5.7730	-2.0813	0.001
	0.5	740	-0.7032	3.4496	-0.9674	0.005
	0.6	650	-1.6964	6.0447	-2.4400	0.012
	0.7	570	-1.8327	6.8387	-2.8806	0.009
	0.8	610	-1.5389	7.0126	-3.0425	0.009
	0.9	650	-1.3158	7.4941	-3.3126	0.014
	1.0	710	-0.1545	6.1400	-2.5100	0.004
NaI-AgI	0.0	940	-2.9944	8.8999	-3.3944	0.002
	0.1	910	-2.0934	6.9509	-2.4402	0.003
	0.2	870	-8.3444	4.4367	-1.3002	0.007
	0.3	840	-1.3786	5.6203	-2.0062	0.001
	0.4	800	-1.7569	6.6342	-2.6650	0.004
	0.5	750	-1.1065	5.6200	-2.2866	0.002
	0.6	720	-0.8230	5.0860	-2.0330	0.004
	0.7	690	-1.0359	5.5800	-2.2639	0.002
	0.8	710	-0.7616	5.3376	-2.2336	0.003
	0.9	790	-0.0466	4.1939	-1.7149	0.002
	1.0	830	0.3339	3.8900	-1.6553	0.003
KI-AgI	0.0	960	-3.1196	6.9625	-2.4749	0.001
	0.1	950	-2.6890	6.1315	-2.1258	0.001
	0.2	930	-2.3677	5.5800	-1.9072	0.001
	0.3	890	-1.8794	4.7892	-1.5875	0.001
	0.4	840	-1.8248	4.8396	-1.6795	0.001
	0.5	770	-1.6482	4.7179	-1.6936	0.001
	0.6	670	-1.5099	4.7706	-1.8021	0.004
	0.7	530	-1.4014	5.0336	-2.0493	0.005
	0.8	520	-1.1203	5.0985	-2.1586	0.006
	0.9	720	0.4882	3.5352	-1.8093	0.007
	1.0	830	0.3339	3.8942	-1.6553	0.003
CsI-AgI	0.0	900	-1.4499	3.2671	-1.0324	0.000
	0.1	860	-1.4774	3.3285	-1.0822	0.003
	0.2	810	-1.4774	3.3570	-1.1203	0.000
	0.3	730	-1.4973	3.4436	1.1886	0.003
	0.4	670	-1.5260	3.5399	-1.2361	0.010
	0.5	590	-1.4371	3.5301	-1.2689	0.002
	0.6	490	-1.2561	3.3685	-1.1948	0.005
	0.7	510	-1.3223	4.0855	-1.6732	0.003
	0.8	600	-0.9338	3.9898	-1.6820	0.004
	0.9	710	-0.4076	3.9324	-1.6980	0.002
	1.0	830	0.3339	3.8942	-1.6553	0.003

Erratum:

For the system NaI–AgI, $x_2 = 0.2$ read $a = -0.8344\ S\,\mathrm{cm}^{-1}$.

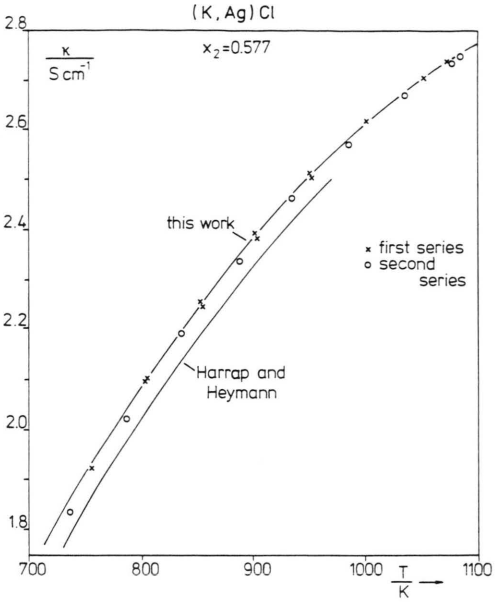

Fig. 2. Electric conductivity of (K, Ag)Cl vs. temperature at $x_{Ag} = 0.577$ compared with data of Harrap and Heymann [10].

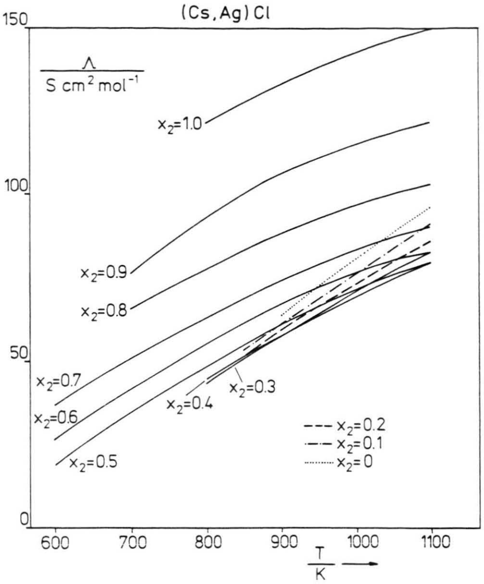

Fig. 3. Equivalent conductivity of (Cs, Ag)Cl vs. temperature for various mole fractions of AgCl.

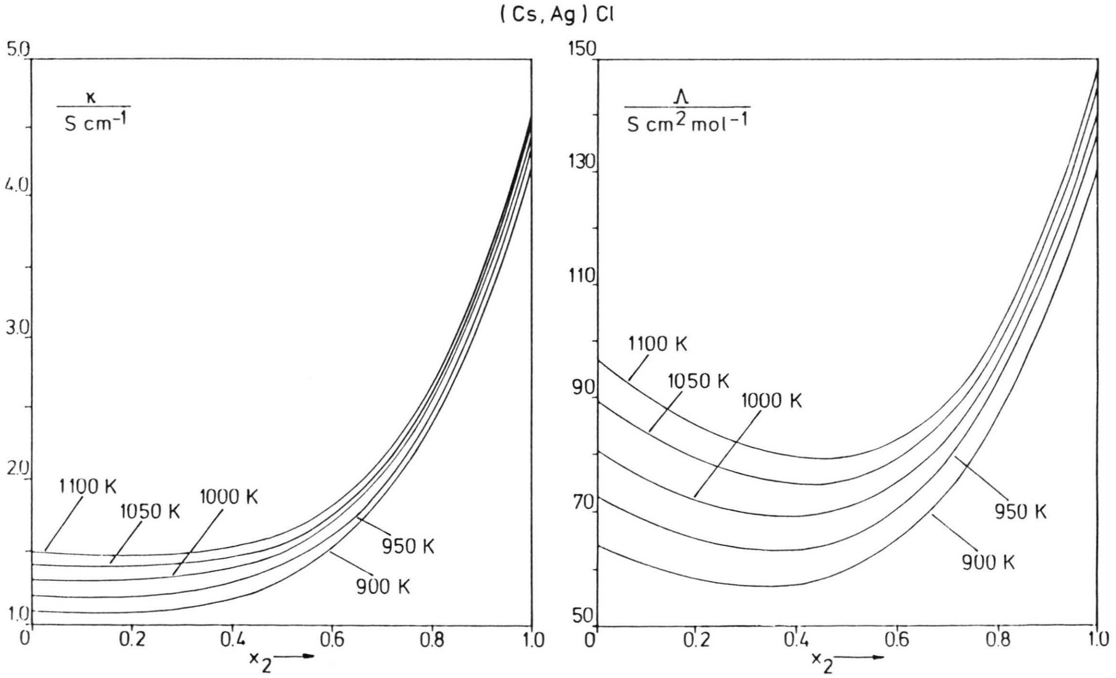

Fig. 4. Specific and equivalent conductivities of (Cs, Ag)Cl as functions of the mole fraction of AgCl at different temperatures.

Table 2. Constants a', b', c', and d' of (4) for the equivalent conductivities for four temperatures. s_{xy} denotes the standard deviation.

System	$\frac{T}{\mathrm{K}}$	$x_{2,\mathrm{min}}$	a'	b'	c'	d'	s_{xy}
			$S\,\mathrm{cm}^2\,\mathrm{mol}^{-1}$				
(K,Ag)Cl	950	0.3	102.8092	-72.1488	94.5104	12.8852	0.543
	1000	0.1	94.9404	8.1094	-43.6178	83.5312	0.874
	1050	0.0	105.1042	-7.5141	-31.2394	80.5174	0.854
	1100	0.0	114.1269	-18.5178	-28.0573	82.7409	1.075
(Cs,Ag)Cl	950	0.0	72.3757	-28.7740	-32.7232	126.5948	0.418
	1000	0.0	80.5364	-32.8943	-40.9942	135.3108	0.464
	1050	0.0	88.4796	-36.6642	-51.6247	145.8159	0.502
	1100	0.0	96.2477	-40.0826	-65.0390	158.4363	0.572
(K,Ag)Br	950	0.2	75.0814	13.7627	-69.9052	100.7576	0.265
	1000	0.1	85.8321	-5.5794	-52.4699	95.0245	0.417
	1050	0.0	95.8950	-24.1582	-34.7753	88.4019	0.724
	1100	0.0	103.5470	-25.8436	-51.0562	101.0272	0.945
(Na,Ag)I	950	0.0	132.4393	-98.8505	88.3923	-12.4200	0.729
	1000	0.0	141.2573	-111.0332	97.7846	-15.8588	0.671
	1050	0.0	149.4909	-120.9678	101.9909	-16.0482	0.697
	1100	0.0	156.9714	-126.0341	91.2862	-4.5322	0.920
(K,Ag)I	950	0.0	85.2940	-45.7867	-6.1978	74.5880	1.646
	1000	0.0	94.2966	-56.9360	1.2575	71.9443	1.485
	1050	0.0	102.6825	-66.4060	5.7238	70.9307	1.296
	1100	0.0	110.5681	-75.0132	9.1518	70.2391	1.181
(Cs,Ag)I	950	0.0	60.7793	-31.2746	-56.8892	135.5647	0.791
	1000	0.0	67.0705	-34.1028	-61.3315	138.8860	0.923
	1050	0.0	73.0256	-36.2456	-67.3578	143.0635	1.088
	1100	0.0	78.8366	-38.5417	-74.0763	147.8959	1.256

Results and Discussion

Table 1 lists the constants a, b, and c of (2) for the six investigated systems for different mole fractions of silver halide. The quality of the fit is expressed by the standard deviation s_{xy}. The third column gives the lowest measured temperature, the highest is always 1100 K. The conductivity values of the systems (K, Ag)Cl at $x_2 = 0.468$, $x_2 = 0.577$, $x_2 = 0.791$, and $x_2 = 1.0$ can be compared with those of Harrap and Heymann [10]. In Fig. 2 the temperature dependent specific conductivities of Harrap and Heymann ($x_2 = 0.577$) are compared with the values from two independent experimental series and the polynomial fit of this work. The deviations are apparently due to the experimental setup: both, the 2-electrode method of Harrap and Heymann as well as their low frequency of 3 kHz lead to higher resistances and thus to lower conductivities.

Our resistances are frequency dependent in the low frequency range. With increasing frequency the measured resistance decreases by different amounts depending on the experimental method and the applied voltage. However, in all cases it converges to the same limiting value at high frequency. In this paper the limiting value at 50 kHz and 50 mV of the 4-electrode method was taken for the calculation of the electric conductivity.

The constants a', b', c', and d' of (4) are listed for 950 K, 1000 K, 1050 K, and 1100 K in Table 2. The polynomial fit (4) describes the concentration dependence between $x_{2,\min}$ (3. column) and $x_2 = 1$. $x_{2,\min}$ is given by the region of validity of the transport numbers [2, 3]. $s_{x,y}$ again denotes the standard deviation. The densities required in (3) for the systems (K, Ag)Cl and (Cs, Ag)Cl have been determined in a previous paper [4] and for the other systems in a just finished work [5].

The temperature dependence of Λ for (Cs, Ag)Cl is plotted in Figure 3. With decreasing silver ion fraction down to $x_2 = 0.4$ the equivalent conductivity and its temperature dependence become smaller. At about $x_2 = 0.4$ this behaviour reverses so that at higher temperatures Λ and $d\Lambda/dT$ increase again.

The concentration dependences of the specific and equivalent conductivities are plotted in Figure 4. The $\varkappa$-value of pure CsCl nearly remains unchanged up to a concentration of about $x_2 = 0.4$, and then it increases to its value in pure AgCl. The equivalent conductivity shows a clear minimum in its concentration dependence and increases steeply on the silver rich side.

Figures 5 and 6 show the concentration dependence of the ionic conductivities in (K, Ag)Cl and (Cs, Ag)Cl at four temperatures. λ_{K^+} is limited by the phase diagram at lower temperatures. λ_{Ag^+} behaves similar in both systems. The ionic conductivities of Ag^+ and Cs^+ in Fig. 6 demonstrate that the steep increase of the conductivity (Fig. 4) for $x_2 > 0.6$ is mainly due to the higher ionic conductivity of the Ag^+-ion in this concentration range. From Fig. 6 it follows that the Ag^+-ions are very mobile in an Ag^+ rich environment whereas they

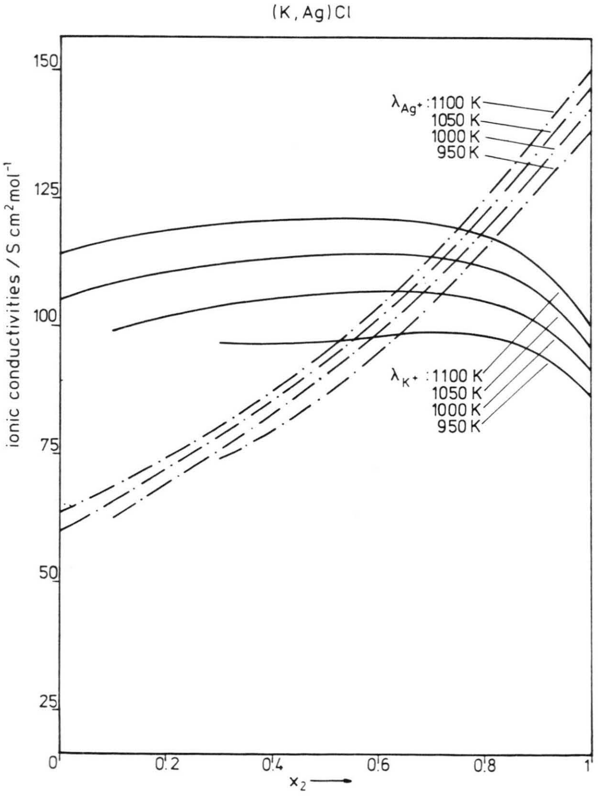

Fig. 5. Ionic conductivities of the silver and potassium ions of (K, Ag)Cl as functions of the mole fractions of AgCl at different temperatures.

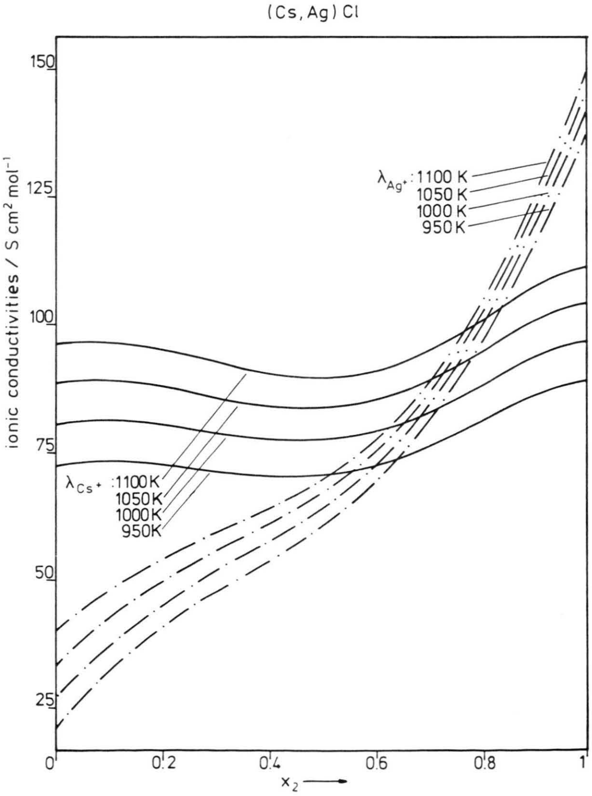

Fig. 6. Ionic conductivities of the silver and cesium ions of (Cs, Ag)Cl as functions of the mole fraction of AgCl at different temperatures.

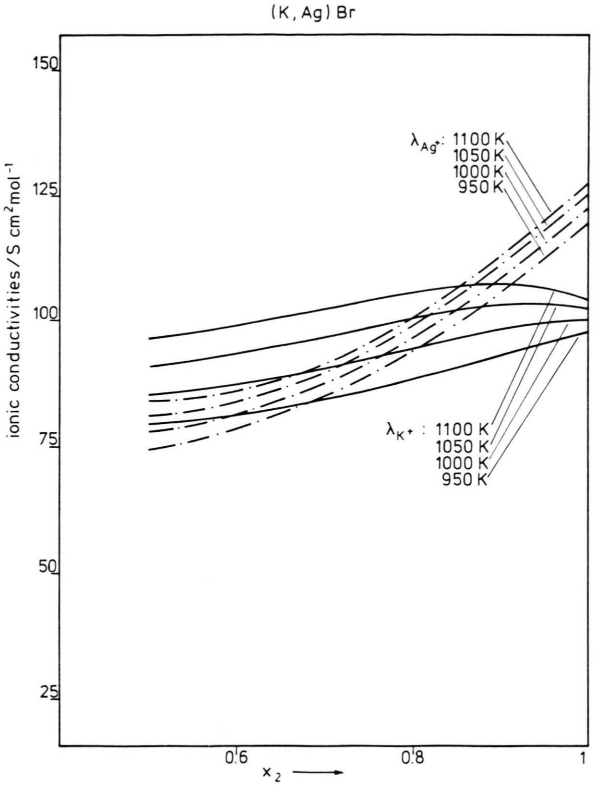

Fig. 7. Ionic conductivities of the silver and potassium ions of (K, Ag)Br as functions of the mole fraction of AgBr at different temperatures.

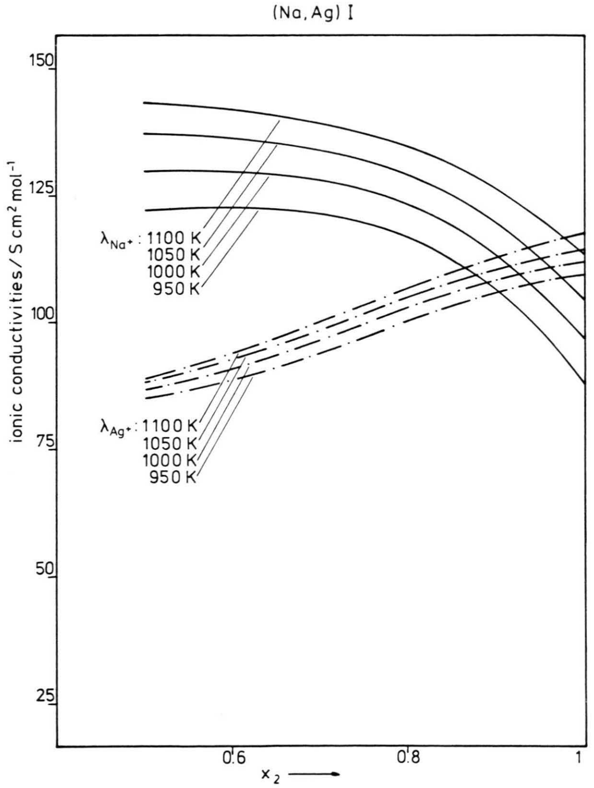

Fig. 8. Ionic conductivities of the silver and sodium ions of (Na, Ag)I as functions of the mole fraction of AgI at different temperatures.

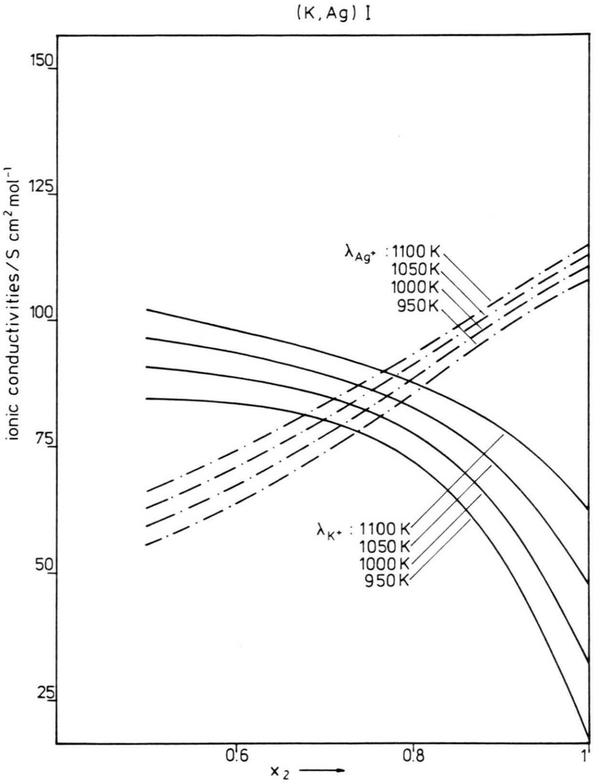

Fig. 9. Ionic conductivities of the silver and potassium ions of (K, Ag)I as functions of the mole fraction of AgI at different temperatures.

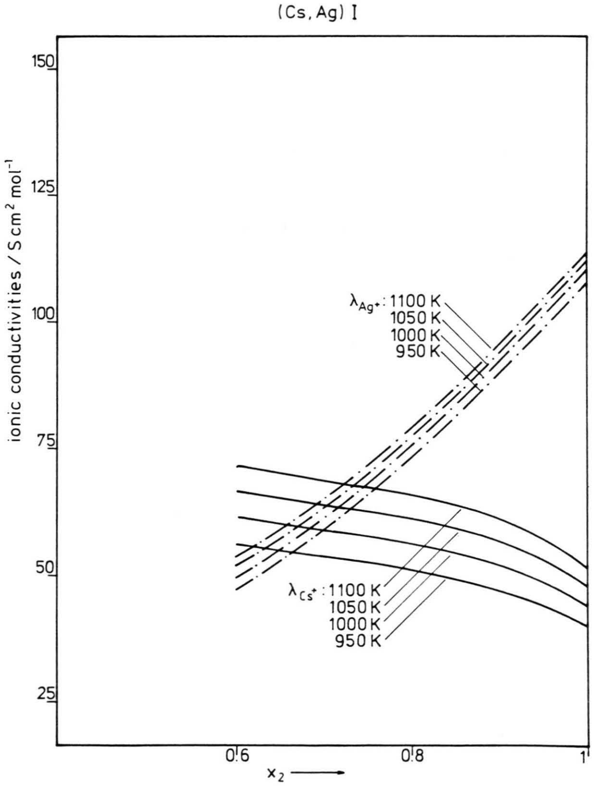

Fig. 10. Ionic conductivities of the silver and cesium ions of (Cs, Ag)I as functions of the mole fraction of AgI at different temperatures.

are much slower in a Cs$^+$ rich environment. The influence of the environment on the Cs$^+$-ions is markedly weaker.

In the system (K, Ag)Br (Fig. 7) this influence is less pronounced but to be seen on the Ag$^+$ rich side.

Figures 8, 9, and 10 show the ionic conductivities of the iodide systems. Here the influence of the environment to the ionic conductivities is again evident.

Acknowledgement

We thank the Minister für Wissenschaft und Forschung des Landes Nordrhein-Westfalen, Düsseldorf, and the Fonds der Chemischen Industrie, Frankfurt, for financial support of this work. The authors would like to appreciate greatly the cooperation with Priv.-Doz. Dr. Tödheide during his stay in Aachen.

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