Conductivities of Binary Molten Alkalihalide/Silverhalide Mixtures

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Dedicated to Karl Heinzinger on the occasion of his 60th birthday

The electric conductivities of molten (Na, Ag)Cl, (Rb, Ag)Cl, (Na, Ag)Br, (Rb, Ag)Br, and (Cs, Ag)Br are determined as functions of composition and temperature from the melting point to 1100 K. The relation of the temperature coefficients to the phase diagram of the systems (K, Ag)Cl, (Rb, Ag)Cl, (Cs, Ag)Cl, and (Cs, Ag)I near and at the phase transition (liquid-solid) is studied. The molar conductivities and mobilities of the cations with reference to the common anion are evaluated.

Introduction

With the new conductivity data given in this paper, the conductivities of all the additive molten alkali metal/silver halides, with the exception of (Rb, Ag)I and the fluorides, are known. This warrants a comparison and discussion of the results. There seems to exist a relation between the temperature dependence of the conductivity near the melting point and the melting point.

Experimental and Results

In [1] and the present work the conductivities of additive molten alkali metal/silver halides were measured. While in [1] the alkali halides were KCl, CsCl, KBr, NaI, KI and CsI, in the present work they are NaCl, RbCl, NaBr, RbBr and CsBr. The experimental setup was the same as in [1], and the new experimental data, relating to the polynominal $\varkappa = a + bT + cT^2$, are listed in Table 1. In (Rb, Ag)I the development of gas made reliable measurements difficult. They are therefore not incorporated in the tables but only illustrated in Figure 1.

Mention should be made of the conductivity measurements of G. Poillerat [2] on the alkali metal/silver bromides. Some deviations from ours are not important for the following discussion.

Discussion

Figures 1–5 refer to a temperature of 1100 K. x_2 is the mole fraction of the silver halide. In Figs. 1 and 2 the conductivities $\varkappa(x_2)$ of the iodides and chlorides are plotted as an example. The greater the alkali cation radius, the smaller is $\varkappa$. There is hardly any change of the conductivity when the silver ion, a good conductor, is added to alkali halides. With the exception of the Na-systems at high concentration of silver the addition of an alkali halide lowers the conductivity.

The greatest halide anion generates the smallest conductivity and the smallest departure from additivity.

The equivalent conductivity is derived from the conductivity and the molar volume [1, 3, 4]. A nearly ideal behaviour of the molar volume is found over the whole concentration range. At 1100 K, the molar excess volume is smaller than ±5%. In Table 1 of [4] the coefficients of the density expansion

$$\varrho(x_2, T) = (\alpha + \beta x_2 + \gamma x_2^2 + \delta x_2^3) + (\alpha' + \beta' x_2 + \gamma' x_2^2 + \delta' x_2^3)\, T \qquad (1)$$

are not given correctly: The units of the primed coefficients are not 10^3 g cm^{-3} but g cm^{-3} K^{-1}, and the value of γ' for (Na, Ag)Br is not -0.76457 but -0.36457. To express the dependence of the equivalent conductivity on the concentration, we used third order polynominals, as in [1]. Table 2 lists the constants and the standard deviation for the system absent in [1].

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Table 1. Constants a, b, and c of $\varkappa = a + bT + cT^2$ 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, N the number of data points.

x_2	$T_{\min}$ [K]	a $[\mathrm{S\,cm^{-1}}]$	$b \cdot 10^3$ $[\mathrm{S\,cm^{-1}\,K^{-1}}]$	$c \cdot 10^6$ $[\mathrm{S\,cm^{-1}\,K^{-2}}]$	s_{xy} $[\mathrm{S\,cm^{-1}}]$	N
(Na, Ag)Cl						
0.1	1045	2.4106	−0.1382	1.2033	0.002	22
0.2	1025	0.3576	3.7129	−0.5908	0.002	26
0.3	975	−2.3050	8.9231	−3.0844	0.003	18
0.4	940	−3.5616	11.7253	−4.5363	0.002	33
0.5	920	−3.0418	11.1563	−4.3720	0.002	22
0.6	885	−2.3737	10.2755	−4.0312	0.002	22
0.7	840	−2.0197	10.0693	−4.0197	0.001	11
0.8	790	−1.4537	9.3637	−3.7142	0.002	22
0.9	760	−1.0999	9.1442	−3.6281	0.004	22
1.0	730	−0.5309	8.3907	−3.2410	0.005	21
(Rb, Ag)Cl						
0.0	990	−3.2445	7.0325	−2.2719	0.002	19
0.1	950	−3.0069	6.7235	−2.1794	0.001	32
0.2	905	−2.9803	6.8523	−2.3006	0.002	22
0.3	840	−2.8958	6.9217	−2.3967	0.002	32
0.4	750	−2.9592	7.3939	−2.6994	0.003	32
0.5	640	−3.0314	8.0418	−3.1158	0.008	32
0.6	525	−2.9688	8.5383	−3.4496	0.006	38
0.7	595	−2.6048	8.6010	−3.5244	0.006	34
0.8	640	−2.1214	8.6947	−3.5890	0.005	32
0.9	680	−1.3782	8.5041	−3.4203	0.004	34
1.0	730	−0.5309	8.3907	−3.2410	0.005	21
(Na, Ag)Br						
0.0	1035	−4.2024	11.2533	−4.1840	0.000	17
0.1	1010	−7.1516	16.7858	−6.8055	0.004	20
0.2	975	−2.3860	8.1142	−2.8903	0.003	23
0.3	940	−2.6647	8.8556	−3.3591	0.002	22
0.4	910	−2.7854	9.1729	−3.5680	0.005	22
0.5	880	−2.2635	8.4353	−3.3301	0.004	22
0.6	835	−1.2941	6.8055	−2.6111	0.002	22
0.7	795	−0.9894	6.6099	−2.6146	0.002	16
0.8	745	−0.8017	6.6173	−2.7012	0.003	22
0.9	710	−0.4313	6.7222	−2.9192	0.016	38
1.0	705	−0.1499	6.3186	−2.6157	0.003	28
(Rb, Ag)Br						
0.0	940	−2.0884	4.7890	−1.5096	0.001	17
0.1	910	−2.2708	5.1967	−1.7337	0.001	22
0.2	870	−2.2463	5.2492	−1.7971	0.001	23
0.3	815	−2.1342	5.1760	−1.8046	0.001	22
0.4	730	−2.2149	5.5657	−2.0524	0.002	22
0.5	600	−2.2108	5.9726	−2.3574	0.009	22
0.6	530	−2.0127	5.9634	−2.4037	0.005	22
0.7	495	−1.8775	6.4445	−2.7236	0.007	16
0.8	575	−1.4340	6.3526	−2.6807	0.007	22
0.9	645	−0.8652	6.3203	−2.7401	0.004	38
1.0	705	−0.1499	6.3186	−2.6157	0.003	28
(Cs, Ag)Br						
0.0	910	−1.8719	4.1654	−1.2980	0.001	21
0.1	840	−1.9651	4.3581	−1.4089	0.001	29
0.2	755	−1.9884	4.4724	−1.4946	0.002	24
0.3	650	−2.0007	4.5803	−1.5752	0.005	24
0.4	550	−1.9644	4.6462	−1.6422	0.003	18
0.5	540	−1.8846	4.7304	−1.7240	0.003	22
0.6	520	−1.8429	5.1079	−1.9795	0.003	22
0.7	525	−1.6856	5.4707	−2.2337	0.005	22
0.8	595	−1.2565	5.5706	−2.3347	0.004	30
0.9	610	−0.7169	5.7659	−2.4373	0.004	22
1.0	705	−0.1499	6.3186	−2.6157	0.003	28

Table 2. Constants (in $\mathrm{S\,cm^2\,mol^{-1}}$) a', b', c', d' of $\Lambda = a' + b'x_2 + c'x_2^2 + d'x_2^3 \pm s_{xy}$ for the equivalent conductivities as functions of the mole fraction x_2 of the silver halide at $T = 1100$ K. s_{xy} denotes the standard deviation.

	a'	b'	c'	d'	s_{xy}
(Na. Ag)Cl	138.1880	−27.1111	46.0708	−9.6058	0.36
(Rb. Ag)Cl	95.2402	−27.0949	−21.8486	101.5860	0.42
(Na. Ag)Br	136.4640	−36.1454	−31.3162	54.9653	0.59
(Rb. Ag)Br	84.0512	−22.2410	−58.5788	123.4220	1.23
(Cs. Ag)Br	80.2756	−31.4776	−50.4827	129.3300	0.36

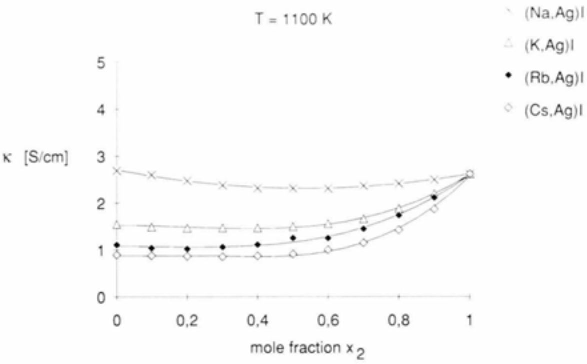

Fig. 1. Specific conductivities of (alkali, silver) iodides as functions of the mole fraction x_2 of the silver iodide at $T = 1100$ K.

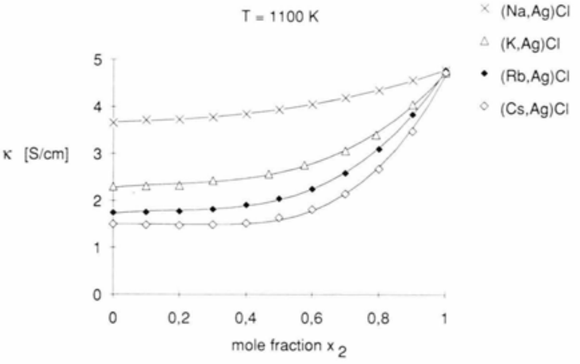

Fig. 2. Specific conductivities of (alkali, silver) chlorides as functions of the mole fraction x_2 of the silver chlorides at $T = 1100$ K.

Isotherms of the equivalent conductivities are plotted in Fig. 3 for a cation row and in Fig. 4 for an anion row. In the three cation rows, there is the same behaviour as for $\varkappa$. In some instances of the four anion rows the functions overlap, especially for the system with the smallest alkali cation (Figure 4).

The internal transport numbers t_1 and t_2 [5–7] connect the internal mobilities of the alkali ion b_1 and

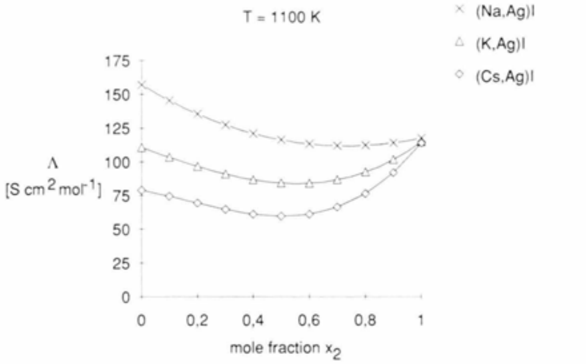

Fig. 3. Equivalent conductivities of (alkali, silver) iodides as functions of the mole fraction x_2 of the silver iodide at $T = 1100$ K for example.

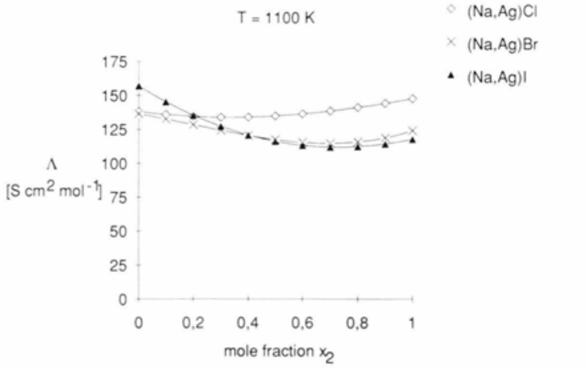

Fig. 4. Equivalent conductivities of (sodium, silver) halides as functions of the mole fraction x_2 of their silver halides at $T = 1100$ K.

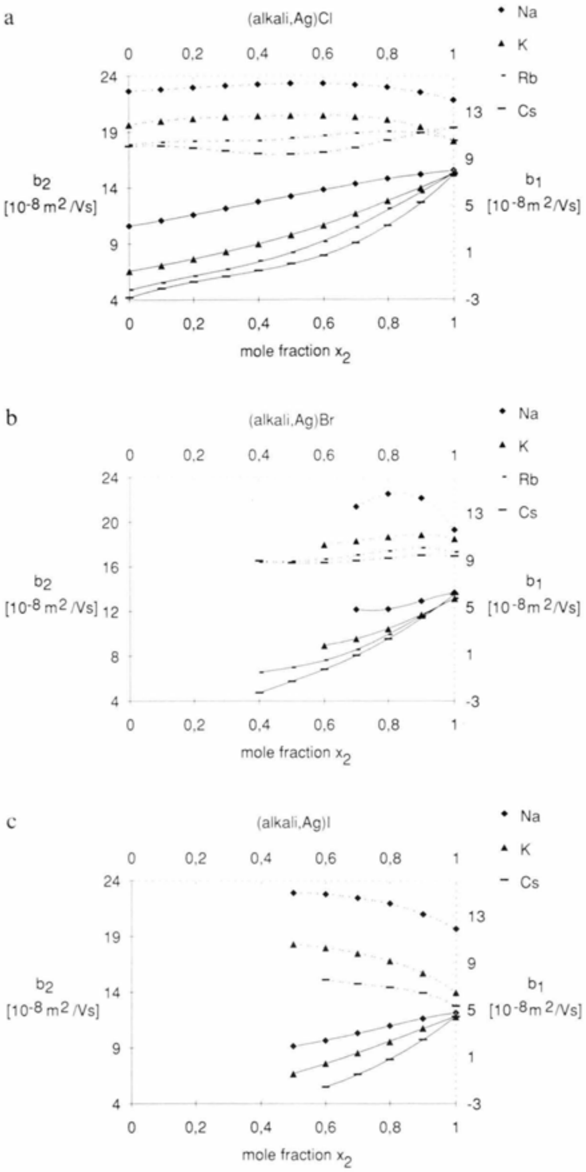

Fig. 5. Mobilities of alkali ions (dotted line) and silver ions (full lines) as functions of the mole fraction x_2 of the silver halide at $T = 1100$ K.

of the silver ion b_2 with the equivalent conductivity according to

$$b_1 = \frac{t_1}{F x_1} \Lambda, \quad b_2 = \frac{t_2}{F x_2} \Lambda, \quad t_1 + t_2 = 1. \tag{2}$$

Experimental reasons often restrict the values to high concentrations of silver [7]. It is very difficult, to measure reliable data of transport numbers in molten salts [8].

The mobility of the silver ion (full lines in Fig. 5) visibly responds to a change of its environment in the molten mixture. The influence of environment on the mobility of the alkali ion far away from the silver side is markedly weaker.

In the high environment, the equivalent conductivity depends on the alkali mobility. Both are only slightly dependent on concentration. In the range with a high concentration of silver, the silver mobility is dominant. Thus, there is a strong influence of concentration on the equivalent conductivity. Because the concentration dependence of the molar volume is nearly linear, we can explain the behaviour of the conductivity in the same way.

Another effect may be of importance: The building of complexes is due mostly to silver ions rather than to alkali ions. The building of complexes reduces the

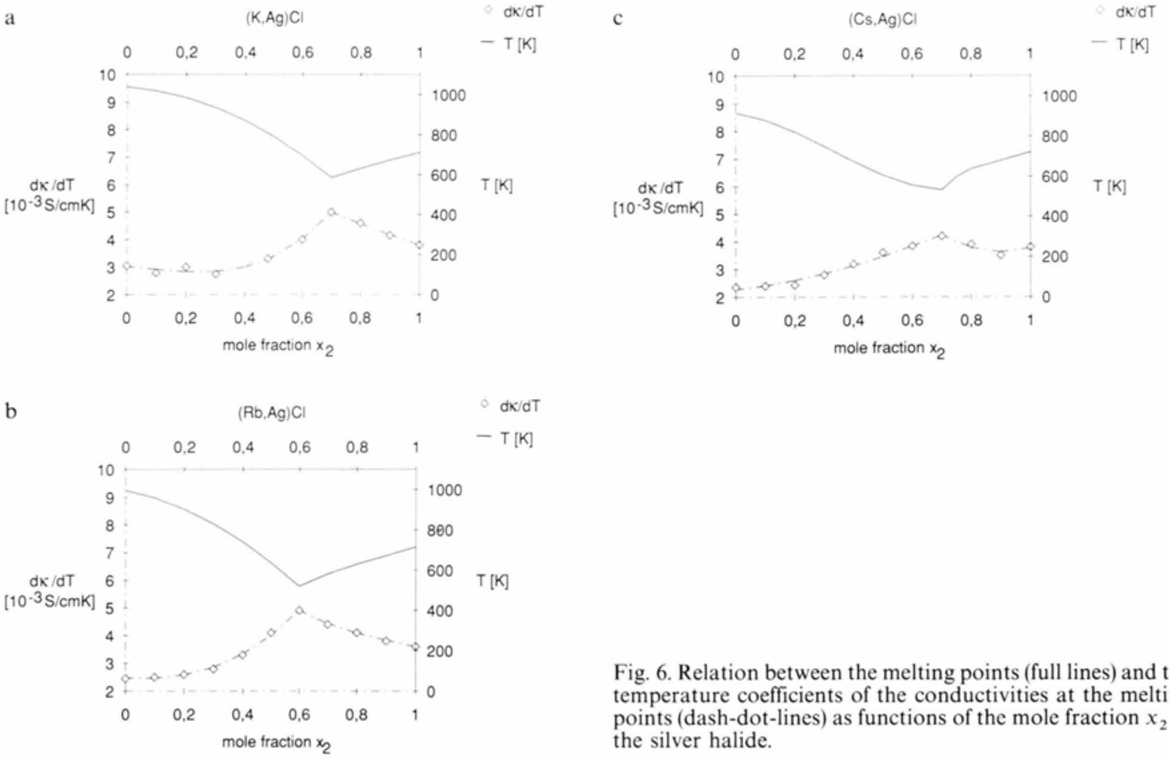

Fig. 6. Relation between the melting points (full lines) and the temperature coefficients of the conductivities at the melting points (dash-dot-lines) as functions of the mole fraction x_2 of the silver halide.

number of charge carriers in the molten salt and leads to a clear decrease in the range with a high concentration of silver.

To calculate the temperature coefficients of $\varkappa$ at the melting point, we extrapolated $\varkappa$ by means of the polynominals of the conductivity. We observed the illustrated relationship for the three examples (K, Ag)Cl, (Rb, Ag)Cl, and (Cs, Ag)Cl (Figures 6a–c). The lower the melting point, the higher is the corresponding temperature coefficient [9]. We will publish further studies near the eutectic mixture.

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