Thermoelectric Power and Electric Conductivity of the (Ag, Na) Cl and (Ag, Na) Br Solid Solutions

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The electric conductivity and the initial thermoelectric power are determined for the solid solutions (Ag, Na) X ($X = Cl, Br$) over the whole composition range.

Data drawn from both kinds of measurements allow to approximately estimate the contributions of cation vacancies and interstitial Ag^+ to the transport process.

Two composition regions are distinguished: $0 \leqq N_{NaX} \leqq 0.6$ and $0.7 < N_{NaX} < 1$ where interstitial Ag^+ and cation vacancies, respectively, are prevailing.

Introduction

Transport phenomena in (Ag, Na) X systems ($X = Cl, Br$) were widely investigated through electric conductivity [1, 2], transport numbers [3, 4], self- and interdiffusion coefficient [5, 6] measurements carried out on pure and doped materials.

On this experimental basis it was established that Ag^+ and Na^+ are the only mobile species, moving via cationic vacancies and interstitial ions.

Contributions of the various mechanisms to transport phenomena were evaluated only for pure NaX [7–9] and AgX [10–13], by adding divalent impurities. The application of this method to the binaries, however, seemed rather difficult as it allowed only to obtain values of cationic vacancy mobilities and their connections with cation jump frequencies for the (AAg, Na) Br system over the composition range $0.7 \leqq N_{NaBr} \leqq 1$ [2, 5].

In the present work such contributions are approximately evaluated by combining electric conductivity and thermoelectric power data.

The "intrinsic behaviour", recognized from electric conductivity at various temperatures above 300 °C, where both systems show a single solid phase over the whole composition range [14], is the object of the discussion.

Experimental

Merck p. a. $AgNO_3$, Merck suprapur NaBr and NaCl, and silver halides precipitated from aqueous $AgNO_3$, thoroughly washed and fully dried in a vacuum oven avoiding any damage by light, were employed.

Pellets (diameter: 8 mm; thickness: 3 or 6 mm for conductivity or thermoelectric power measurements respectively) were obtained by pressing (under 3 – 4 ton/cm²) between silver powder (200 mesh) layers the previously melted (under inert atmosphere) and grounded appropriate powder mixtures. Further, they were annealed at 400 °C for 24 – 36 hours to obtain homogeneous solid solutions.

The conductivity was measured by means of an autobalancing Wayne-Kerr bridge mod. B 331 (10^4 rad/sec frequency) on pellets held under inert atmosphere between steel electrodes bored to contain chromel-alumel thermocouples.

The experimental equipment for the thermoelectric power measurements was described in a previous paper [15]; a potentiometric voltmeter Keithley mod. 630 was employed for V measurements. From the linear plots of the thermal emf, V, *vs* ΔT ($\Delta T \leqq 10\ °C$), the values of $\varepsilon = dV/dT$, at various T, were obtained.

The specimens employed can be considered sufficiently pure in view of the aim of the present work, the impurity content being possibly estimated from the values of the intrinsic-extrinsic transition temperatures.

Results and Discussion

The conductivity values, σ, satisfactorily agree with previous data [1, 13, 16].

At each composition a plot of $\log \sigma T$ *vs* $1/T$ allows to recognize an "intrinsic range" extended from the melting point to a temperature where the slope of the straight line fitting the experimental data abruptly changes. For the pure components, such a "knee" is usually interpreted as the transition point from the intrinsic to the extrinsic structural disorder.

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In the present systems, as a rule, the above plots show two singular points: that at higher temperature still corresponds to the intrinsic-extrinsic transition, the other to the demixing temperature of the solid solutions.

However, for a few compositions of the (Ag, Na) Br system one knee only was detected, very close to the demixing temperature determined by X-ray diffraction measurements[14]: in such cases there is a direct transition from an intrinsic single phase to a demixed system.

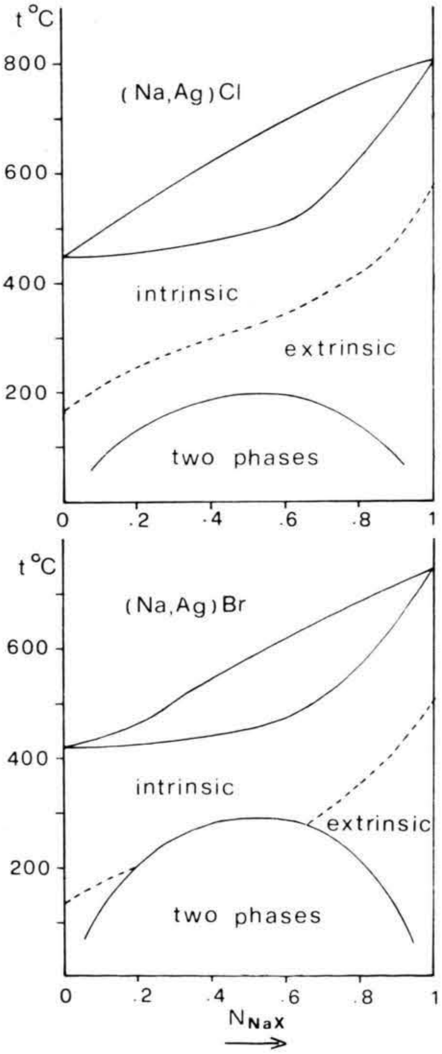

Fig. 1. Phase diagrams of the (Ag, Na) X systems; solidus-liquidus curves are reported from literature[14]; intrinsic-extrinsic transitions and demixing temperatures are detected through conductivity measurements.

Figure 1 represents the phase diagrams where the intrinsic-extrinsic transitions and demixing temperatures are evidenced.

At higher temperatures, the plots $\log \sigma T$ *vs* $1/T$ for pure silver halides and for a few solid solutions at low NaX content show a deviation from the intrinsic straight line, a phenomenon interpreted, in the case of AgCl and AgBr, as due either to an abnormal lattice expansion or to a Debye-Hückel interaction[12, 13].

Anyway, for every composition, the intrinsic σ data (above 300 °C) can be fitted by equations of the type:

$$\log \sigma T = \log \sigma_N{}^0 - Q_N/RT \qquad (1)$$

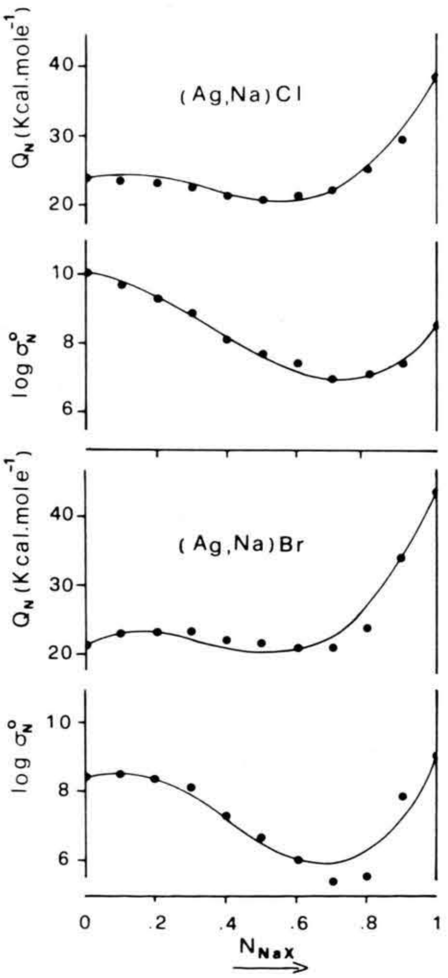

Fig. 2. Activation energy, Q_N (upper curve), and preexponential T-independent factors, $\sigma_N{}^0$ (lower curve), according to the equations given in the text, are reported along with the experimental values for both (Ag, Na) X systems.

where the subscript "N" refers to composition (molar fraction of NaX).

The Q_0 and $\log \sigma_0{}^0$ values for the Ag halides are 21.7 kcal/mole and 8.32 for AgCl, and 23.7 kcal/mole and 10.04 for AgBr: these values can be compared with those obtained from Müller's data, over the same temperature range, according to Eq. (1), i. e., 21.1 kcal/mole and 8.12 for AgCl, and 23.7 kcal/mole and 10.31 for AgBr.

Q_1 and $\log \sigma_1{}^0$ for the alkali halides are 44.5 kcal/mole and 8.58 for NaCl, and 39.1 kcal/mole and 9.12 for NaBr.

As for the intermediate compositions the values of the same quantities can be well fitted, as shown in Fig. 2, by the following equations:

$$(\mathrm{Ag, Na})\mathrm{Cl} \begin{cases} Q_N = Q_0 + N(Q_1 - Q_0) - 99.8\, N^2 (1-N)\,, \\ \log \sigma_N{}^0 = \log \sigma_0{}^0 + N(\log \sigma_1{}^0 - \log \sigma_0{}^0) - 16.1\, N^2(1-N)\,; \end{cases}$$

$$(\mathrm{Ag, Na})\mathrm{Br} \begin{cases} Q_N = Q_0 + N(Q_1 - Q_0) - 84\, N^2 (1-N)\,, \\ \log \sigma_N{}^0 = \log \sigma_0{}^0 + N(\log \sigma_1{}^0 - \log \sigma_0{}^0) - 12.8\, N^2(1-N)\,. \end{cases}$$

In the literature, no thermoelectric power data are reported for cells of the type:

$$\mathrm{Ag}_T/(\mathrm{Ag, Na})\mathrm{X}_{(s)}/\mathrm{Ag}_{T+\Delta T}$$

while there is a number of such investigations about the Ag halides[17–19]; the values reported in the present work show a favourable agreement with other authors results.

For the above cell the thermoelectric power, ε, is expressed as[20, 21]:

$$F\,\varepsilon = S_{\mathrm{Ag}} - \overline{S}_{\mathrm{Ag}^+} - \sum_i t_i\, Q_i{}^*/T \qquad (2)$$

where F = Faraday's constant; S_{Ag} = molar entropy of metallic Ag; $\overline{S}_{\mathrm{Ag}^+}$ = partial molar entropy of Ag^+ in the solid solution; t_i and $Q_i{}^*$ are respectively the number and the heat of transport for the i^{th} mobile ion. As for the term $\overline{S}_{\mathrm{Ag}^+}$ it is possible to assume in a first approximation:

$$\overline{S}_{\mathrm{Ag}^+} = S^0_{\mathrm{Ag}^+} - R \ln N_{\mathrm{Ag}^+} \qquad (3)$$

where $S^0_{\mathrm{Ag}^+}$ = partial molar entropy of Ag^+ in the pure silver halide and N_{Ag^+} = molar ratio. In Eq. (3) the excess term $\overline{S}^{\,\mathrm{e}}_{\mathrm{Ag}^+}$ is negligible[14]. $S^{\,0}_{\mathrm{Ag}^+}$ can be evaluated from S_{AgX}[22] according to Pitzer's relation[23]:

$$S^0_{\mathrm{Ag}^+} = 1/2\,(S_{\mathrm{AgX}} + 3/2\, R \ln M_{\mathrm{Ag}}/M_{\mathrm{X}})\,. \qquad (4)$$

Thus, from Eqs. (2), (3) and (4) it is possible to obtain the quantity $\sum_i t_i\, Q_i{}^*$.

In Tabl. 1 and 2 the experimental ε's, determined at various T's in the intrinsic range, are reported along with the corresponding $(\sum_i t_i\, Q_i{}^*)$'s. As an example, Fig. 3 shows the plots ε *vs* N_{NaBr} and $\sum_i t_i\, Q_i{}^*$ *vs* N_{NaBr}, at various T's. In the case of compositions close to pure NaX, the values of the quantity $\sum_i t_i\, Q_i{}^*$ correspond to ε values extrapolated from the intrinsic range: in Tabs. 1 and 2 such data are reported in brackets and must be considered just as merely indicative.

In the following the results are discussed on the basis of the suggestions proposed by some authors for (Ag, Na)Br[2, 5].

Table 1. Themoelectric power experimental data, $F\varepsilon$ (cal/mole degree), and cationic overall heat of transport $\sum_i t_i\, Q_i{}^*$ (kcal/mole) obtained from Eq. (2) for the system (Ag, Na)Cl.

	T = 350 °C		T = 400 °C		T = 450 °C		T = 500 °C	
N_{NaCl}	$F\varepsilon$	$\sum_i t_i\, Q_i{}^*$	$F\varepsilon$	$\sum_i t_i\, Q_i{}^*$	$F\varepsilon$	$\sum_i t_i\, Q_i{}^*$	$F\varepsilon$	$\sum_i t_i\, Q_i{}^*$
0.0	−21.0	10.9	−16.6	8.7	−12.7	6.6	–	–
0.1	−18.8	9.4	−16.1	8.3	−12.9	6.6	–	–
0.2	−18.4	9.1	−16.4	8.3	−13.8	7.1	–	–
0.3	−17.5	8.3	−16.4	8.1	−14.2	7.1	–	–
0.4	−16.6	7.6	−15.7	7.4	−14.3	7.0	–	–
0.5	−18.7	8.6	−16.4	7.6	−14.1	6.6	−11.5	5.0
0.6	−18.6	8.3	−16.1	7.2	−14.1	6.2	−12.0	5.0
0.7	(−14.3)	(5.3)	−12.4	4.3	−10.6	3.3	− 8.9	2.2
0.8	–	–	–	–	(− 5.1)	(−1.2)	− 5.5	−1.0
0.9	–	–	–	–	–	–	(− 5.0)	(−2.5)

Table 2. Thermoelectric experimental data, $F\varepsilon$ (cal/mole degree), and cationic overall heat of transport $\sum_i t_i Q_i^*$ (kcal/mole) obtained from Eq. (2) for the system (Ag, Na) Br.

	$T = 350$ °C		$T = 400$ °C		$T = 450$ °C		$T = 500$ °C	
N_{NaBr}	$F\varepsilon$	$\sum_i t_i Q_i^*$	$F\varepsilon$	$\sum_i t_i Q_i^*$	$F\varepsilon$	$\sum_i t_i Q_i^*$	$F\varepsilon$	$\sum_i t_i Q_i^*$
0.0	−14.3	6.5	−11.3	4.8	—	—	—	—
0.1	−13.2	5.7	−10.8	4.3	—	—	—	—
0.2	−13.5	5.7	−11.5	4.6	—	—	—	—
0.3	−13.8	5.7	−11.5	4.5	− 9.4	3.2	—	—
0.4	−12.9	5.0	−11.6	4.3	−10.3	3.6	—	—
0.5	−13.4	5.0	−12.2	4.5	−11.1	3.9	—	—
0.6	−13.1	4.6	−12.0	4.0	−10.6	3.2	—	—
0.7	−11.3	3.2	−10.8	2.8	−10.1	2.5	−9.2	1.8
0.8	—	—	(− 7.5)	(0.1)	− 7.4	−0.1	−8.3	0.5
0.9	—	—	(− 5.0)	(−2.5)	− 4.8	−2.9	−4.5	−3.5

It is well known that the components AgX and NaX show different intrinsic disorders, i.e. Frenkel's for AgX and Shottky's for NaX; thence cationic and anionic vacancies and Ag^+ interstitial ions are to be considered the main lattice defetcts while Na^+ interstitials may be reasonably neglected.

Furthermore, the cations only are mobile and their transport occurs via interstitial Ag^+ and cationic vacancies (denoted by ○ and □ respectively).

With these assumptions, the electric conductivity can be expressed as

$$\sigma = \sigma_\bigcirc + \sigma_\square = \sigma^0_\bigcirc/T \exp\{-Q_\bigcirc/RT) + \sigma^0_\square/T \exp\{-Q_\square/RT\} \tag{5}$$

where $\sigma_\bigcirc$ and $\sigma_\square$ are the partial conductivities of interstitials and cationic vacancies; the activation energies, $Q_\bigcirc$ and $Q_\square$, represent the formation energy plus the generally smaller migration term of the corresponding defect; $\sigma^0_\bigcirc$ and $\sigma^0_\square$ are T independent factors, which also contain formation and migration terms.

In turn, the quantity $\sum_i t_i Q_i^*$ may be expressed as:

$$\sum_i t_i Q_i^* = t_\bigcirc Q^*_\bigcirc - t_\square Q^*_\square \tag{6}$$

where $t_\bigcirc = \sigma_\bigcirc/\sigma$ and $t_\square = \sigma_\square/\sigma$ are the defect transport numbers, while $Q^*_\bigcirc$ and $Q^*_\square$ represent the overall heats of transport, which contain a formation term and the reduced heat of transport.

In both relations (5) and (6) the quantities concerning cationic vacancies are, for a limited temperature range, average values since they refer to the transport (via vacancies) of two distinct cation types.

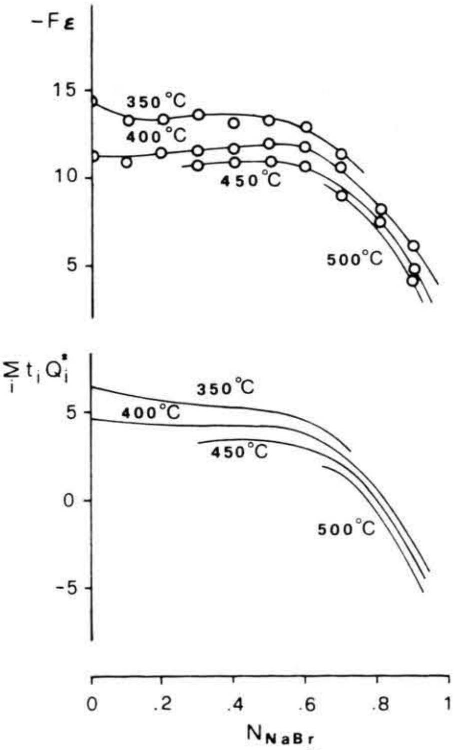

Fig. 3. Thermoelectric power experimental values, $F\varepsilon$, (cal/mole deg), and the sum $\sum_i t_i Q_i^*$ (kcal/mole) are reported for the system (Ag, Na) Br.

From Figs. 2 and 3 and Tabs. 1 and 2 it is possible to recognize in both systems two regions: the first corresponding to compositions $0 \leqq N_{\mathrm{NaX}} \leqq 0.6$, where the Q_{N} values (Fig. 2) show a small scattering ($\pm 10\%$) about the mean ones observed for the pure Ag halides, and the quantity $\sum_i t_i Q_i^*$ is substantially composition independent; and the second one (for $N_{\text{NaX}} > 0.6$), where Q_N increases steeply, whereas $\sum_i t_i Q_i^*$ decreases and finally takes negative values.

As for the first region, it was established that the Ag^+ transport number is very close to 1 [3, 4]. Thence the total conductivity of these solid solutions must be due to a single ion migrating via two distinct mechanisms; nevertheless, the experimental σ values are very well fitted by Eq. (1), a fact which may be justified, as suggested by Jost for the pure Ag halides, assuming that the term Q_N in Eq. (1) represents an appropriate average of the quantities $Q_\circ$ and $Q_\square$ of Equation (5).

Furthermore on theoretical [23, 24] and experimental [19, 25, 26] grounds it was shown that the values of the migration energy and of the reduced transport heat are close to each other; then, it may be assumed that $Q_\circ^* \approx Q_\circ$ and $Q_\square^* \approx Q_\square$ and that the quantity $\sum_i t_i Q_i^*$ (which in this region corresponds to the Ag^+ overall heat of transport) may be expressed in a rough approximation as:

$$\sum_i t_i Q_i^* = Q_{\text{Ag}}^* + = (t_\circ - t_\square) Q_N \,. \tag{7}$$

Equation (7) allows to account for the order of magnitude of the defect transport numbers.

At $T = 400\ °\text{C}$, the $t_\circ$ values [0.6 for (Ag, Na)Br and 0.7 for (Ag, Na)Cl], obtained in the above way, do not change with composition and agree with Teltow's data [10] on pure Ag-halides, while they are $10 - 15\%$ smaller than those evaluable from other authors results [12, 17].

Our results suggest that in the region $0 \leqq N_{\text{NaX}} \leqq 0.6$ the transport mechanisms effective in the pure Ag halides are also present in the solid solutions in the same extent; the intrinsic structural disorder too should reasonably be of the same type as in pure silver salts.

As for the second composition region, Fig. 3 shows that, at about 500 °C (where the behaviour of these solid solutions is undoubtedly intrinsic) the quantity $\sum_i t_i Q_i^*$ decreases rapidly and for $N_{\text{NaX}} \geqq 0.8$ assumes negative values. This behaviour may be simply explained taking into account that the cationic vacancies term, $-t_\square Q_\square^*$, in Eq. (6) is negative; furthermore, since at these temperatures in pure Na-halides the mobile species is the cation, which migrates via cationic vacancies, the behaviour of $\sum_i t_i Q_i^*$ is the expected one.

Thus it may be suggested that the cationic vacancies contribution to the transport process is predominant for $0.8 \leqq N_{\text{NaX}} \leqq 1$.

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