Influence of Dissolved Silver on the Electrical Conductivity and the Optical Spectra of the Molten Mixtures $AgCl_{1-x}Br_x$

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Electrical conductivities of molten mixtures $AgCl_{1-x}Br_x$ were measured at different temperatures. No influence of dissolved silver on the conductivity could be detected. The apparent energy of activation does not depend linearly on x. The optical spectra of molten mixtures $AgCl_{1-x}Br_x$ show a flat absorption edge which can be treated by the formalism of Urbach. The energy gap of the indirect transition can be evaluated as a function of x. In metal-containing mixtures, the edge is slightly red shifted. This red shift can be attributed to a new absorbing species. The results make it likely that the interaction between the dissolved metal and the melt is of the charge transfer type.

1. Introduction

In two earlier papers [1, 2] we reported on the solubility of the Ib-metals silver and copper in their corresponding chloride-bromide-melts. It could be shown that the enthalpy and entropy of dissolution depend in a non-monotonous way on the composition of the melt. Up to now such a behaviour was unknown in metal-molten salt systems.

Usually metal-molten salt systems have been classified into two different categories:

a) Systems of the Bi-$BiCl_3$-type, where a redox reaction between the dissolved metal and the cation of the melt takes place and the electrical conductivity and its temperature coefficient are of the same order of magnitude as in concentrated ionic solutions [3].

b) Systems of the alkali-alkali halide type, having properties which can be described by the concept of nearly free electrons [4]. In these solutions excess electrons are present, occupying anion vacancies in the "lattice" of the melt (F-centers) [5].

The observed dependence of the dissolution effects on the composition of the Ag-halide melts cannot be explained by one of these models. Further investigations should give more information on the state of the dissolved Ib-metals in the mixed melts and on the metal-molten salt interaction. In the following we report on measurements of the electrical conductivity and optical absorption of molten silver chloride-silverbromide mixtures containing dissolved silver. If nearly free electrons were present in these solutions a pronounced increase in electrical conductivity with increasing metal concentration should be observed. A comparison of the absorption spectra of these melts with the known spectra of excess electrons in alkali halides [6] should give further information.

2. Experiments

2.1. *Conductivity Measurements in Ag-$AgCl_{1-x}Br_x$ Melts*

Resistance measurements were made with a Wayne-Kerr-Universal-Bridge 224, connected with a RC-Generator (Sub 40870, Rohde and Schwarz) supplying the bridge with a.c. of 25 kHz. The electrodes consisted of graphite (Firma Ringsdorff). Resistances ranging from 50 to 100 Ω were obtained with the fused quartz conductivity cell shown in Figure 1.

Each electrode compartment contained a Ni-NiCr-thermocouple protected by a quartz tubing. The quartz tubings were arranged at different heights in order to detect temperature gradients. These gradients werde caused by heat losses due to the high thermal conductivity of the graphite electrodes. In order to eliminate the gradients additional heating elements were placed at the electrode compartments. The cell constants were determined in the usual way by calibration with 1 n KCl-solution at room temperature, accounting for thermal expansion of the quartz capillaries. In order to

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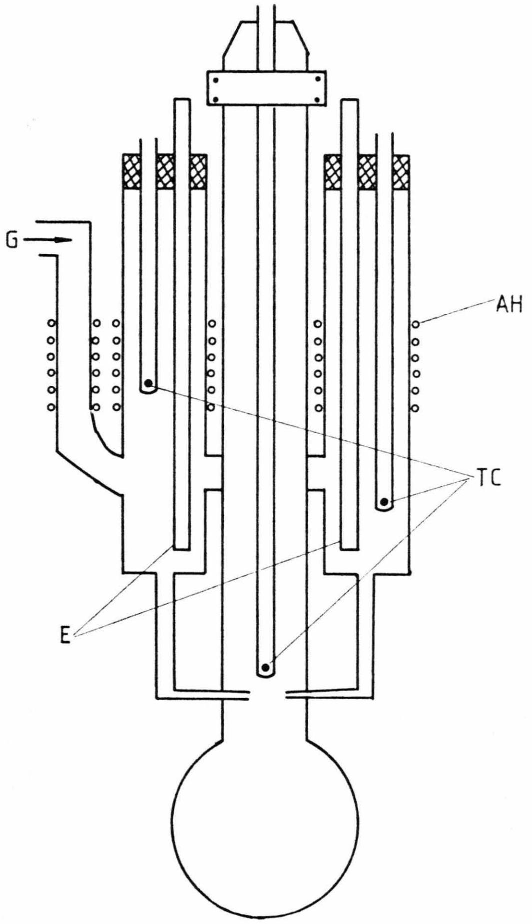


Fig. 1. Conductivity cell (AH: additional heating, E: graphite electrodes, G: gas inlet, TC: thermocouples).

obtain a desired fraction x, calculated masses of the halides were weighed into the cell. Afterwards the cell was evacuated, filled with argon and heated in an electric furnace. Temperatures were measured with a Ni-NiCr thermocouple in the central compartment of the cell.

After measuring the resistance of silver free melts a small silver rod of 99.99% purity was added to the melt thus producing a saturated solution of silver, the resistance of which was measured in the usual way.

2.2. *Spectroscopic Investigations*

Absorption spectra were measured using a Zeiss spectrophotometer PMQ II which was modified for high temperature performance. The monochromator was positioned between sample and detector, thus shielding the detector from thermal radiation. Figure 2 shows the experimental arrangement.

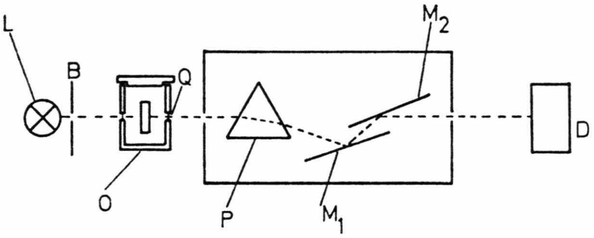


Fig. 2. Optical arrangement (B: blend; D: detector; L: light source; M_1 and M_2: optical mirrors; O: furnace; Q: quartz windows; P: monochromator).

Special optical cells had to be constructed because of the very corrosive nature of the molten salts and their high absorption constants. They consisted of two small flat quartz plates (12 × 20) mm², 1 mm in thickness, which were separated by a quartz filament of 70 μm in diameter. The melt was kept in between the plates by capillary forces.

The cuvettes were heated to the desired temperatures in an electric furnace. Spectra of metal free melts were measured against air as reference. For silver-containing melts a sample of the pure halide was used as reference.

To control the whole arrangement the spectrum of the Co^{2+}-ion in a LiCl-KCl eutectic melt was measured and compared with literature data [7]. The agreement was satisfying.

3. Results

3.1. *Electrical Conductivities*

Figures 3 and 4 show the experimental results for the pure melts AgCl and AgBr. In the latter case, our results fit well into the elder data, only the temperature dependence seems to be higher in our experiments. In the case of AgCl, it is not only the temperature dependence, but also the absolute values of the conductivity which differ from the literature data. It is known that AgCl in the molten state is a very aggressive material. With high temperature glasses, ion exchange leads to the presence of divalent cations in the melt. Platinum is resistant to molten AgCl only if no chlorine is present. At elevated temperatures, when the dissoziation of AgCl becomes detectable, platinum is attacked by the melt. The marked influence of divalent cations on the conductivity is shown by curve e: the crosses represent experimental points, which we obtained

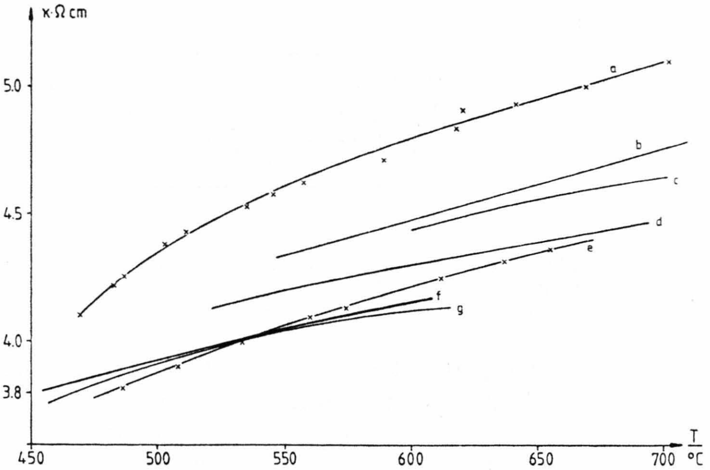


Fig. 3. Temperature dependence of the electrical conductivity of molten AgCl. a) this work; b) K. Arndt and A. Gessler, Z. Elektrochem. **14**, 662 (1908); c) R. Lorenz and A. Höchberg, Z. anorg. Chem. **94**, 305 (1916); d) H. Winterhager und L. Werner, Forschungsberichte des Wirtschafts- und Verkehrsministeriums des Landes Nordrhein-Westfalen Nr. 341 (1956); e) × this work, AgCl + 1 mole % $CdCl_2$; full line: B. S. Harrap and E. Heymann, Trans. Faraday Soc. **51**, 259 (1955); f) C. Tubandt and E. Lorenz, Z. Phys. Chem. **87**, 513 (1914); g) K. Sakai, J. Chem. Soc. Japan **75**, 182 (1954).

with a silver chloride melt containing 1 mole % $CdCl_2$, while the curve represents experimental data, obtained using a glass cell. The impurity effects on the conductivity of molten silver chloride are under investigation now in our laboratory.

Concerning the temperature dependence, it should be pointed out, that our results in the case of AgBr extrapolate to a recently measured value of $\varkappa = 3.4\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at 733 °C [8]. As temperature gradients in the melt were carefully avoided in our experiments we feel that the results should be reliable.

From Fig. 5, two important results can be seen: The experimental data for $\varkappa(T)$ can be parametrizised using an Arrhenius-type equation

$$\varkappa = \varkappa_0 \exp[-E_\varkappa / R T]. \tag{1}$$

Furthermore, no influence of dissolved silver on the conductivities of the melts can be detected. Both findings are not only valid for the pure halides AgCl and AgBr but for the total composition range $AgCl_{1-x}Br_x$. The experimental results therefore can be most economically represented by giving $\varkappa_0$ and $E_\varkappa$ as functions of x as is done in Figure 6.

3.2. *Optical Spectra*

For all temperatures and compositions the absorption spectra of pure $AgCl_{1-x}Br_x$ melts exhibit a structureless, flat absorption edge which is shifted to higher wave numbers with decreasing x (Figure 7).

The flattening of the curves at absorbances $A = \log I_0/I > 2$ is due to the low sensitivity of the instrument. In Fig. 8 photon energies and wave numbers at constant absorption coefficient ($K = A/d = 100\ \mathrm{cm}^{-1}$, with d: optical path length) are plotted as a function of melt composition. Figure 8 includes data from literature [9] for the mixed crystals.

The spectrum of a silver saturated solution measured against the pure halide exhibits a structureless band (Fig. 9), the hight of which is proportional to the concentration of the dissolved silver (Figure 10). With increasing temperature the band maximum is shifted to lower energies.

The half widths of these bands are smaller than those of *F*-center like electrons in molten alkalihalides by a factor of four but are of the order of magnitude typical for charge transfer bands.

In Table 1 the results of the spectroscopic investigations are listed, where $\tilde{\nu}_{\max}$, $\varepsilon_{\max}$ are the wave-number and the molar extinction coefficient of the band-maximum, respectively. $\tilde{\nu}_{1.5}$ is the wave-number where the absorption edge of the silver free melts reaches the value $A = \log I_0/I = 1.5$. All data refer to 500 °C.

Tab. 1. Absorption spectra of Ag-Ag(Cl, Br)-melts.

x_{AgBr}	$\tilde{\nu}_{\max}/\mathrm{cm}^{-1}$	$\varepsilon_{\max}/$ $(\mathrm{l\ mol}^{-1}\ \mathrm{cm}^{-1})$	$\tilde{\nu}_{1,5}/\mathrm{cm}^{-1}$
0.0	22200	4000	21640
0.1	—	—	19760
0.2	19330	2750	19790
0.4	20570	1800	19520
0.5	20450	1400	—
0.6	—	—	19190
0.8	18910	6300	18710
1.0	19220	1300	18480

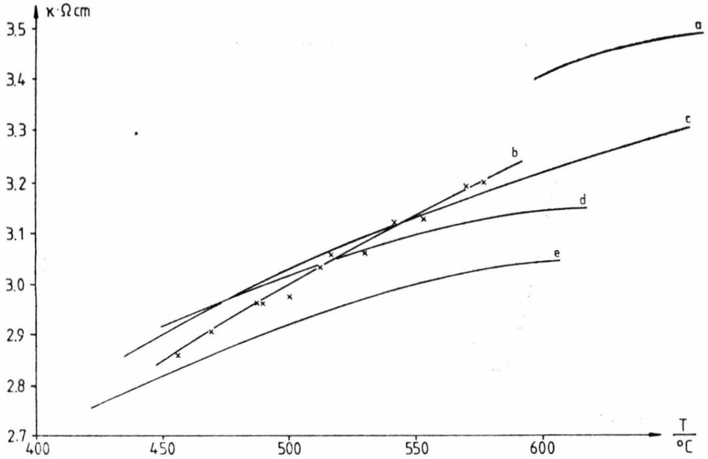
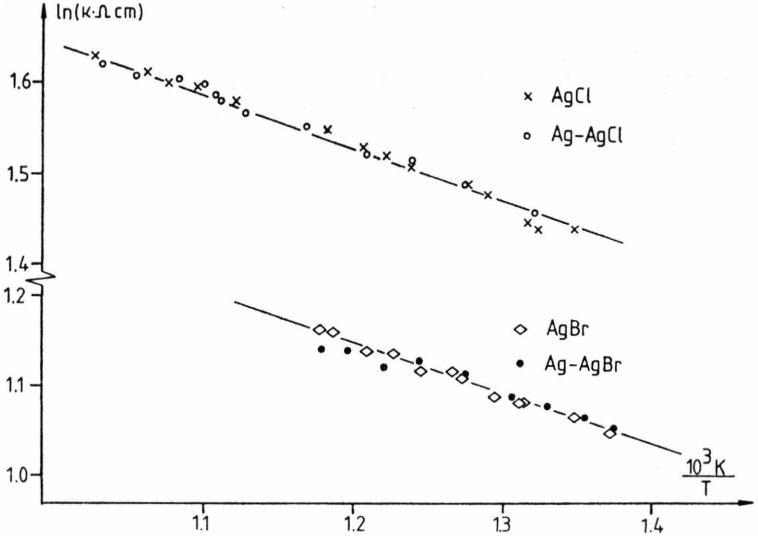


Fig. 4. Temperature dependence of the electrical conductivity of molten AgBr. a) R. Lorenz and A. Höchberg, Z. anorg. Chem. **94**, 305 (1916); b) this work; c) B. S. Harrap and E. Heymann, Trans. Faraday Soc. **51**, 259 (1955); Y. Doucet and M. Bizouard, Comt. Rend. **250**, 73 (1960); d) K. Arndt and A. Gessler, Z. Elektrochem. **14**, 662 (1908); e) C. Tubandt and E. Lorenz, Z. Phys. Chem. **87**, 513 (1914).



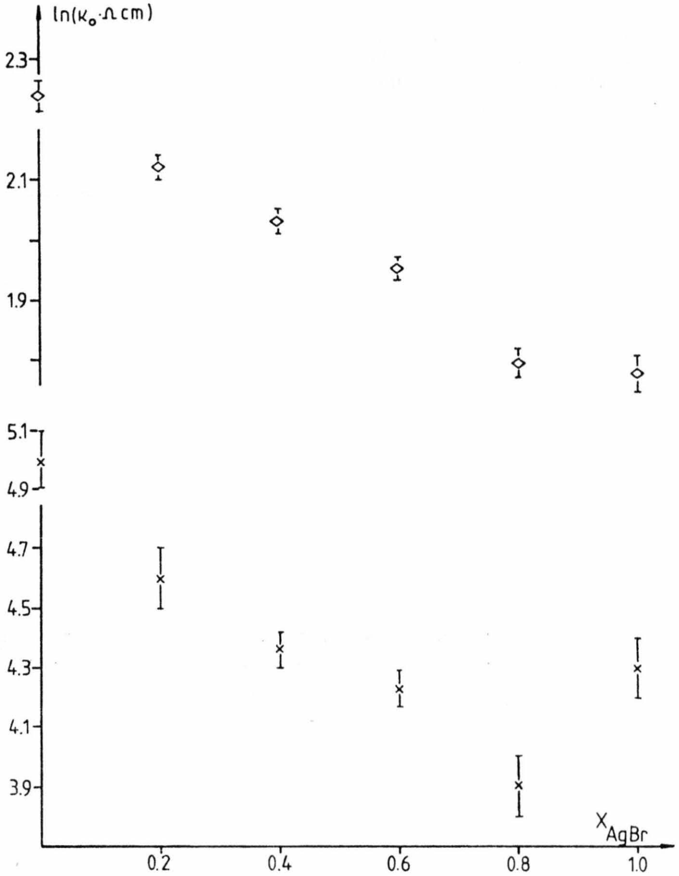


Fig. 6. $E_\varkappa$ and ln $\varkappa_0$ from Eq. (1) vs · x_{AgBr}. $E_\varkappa$ in kJ · mol^{-1}.

Fig. 5. ln $\varkappa$ vs. $1/T$ for the pure molten salts AgCl and AgBr and for the saturated solutions of silver.

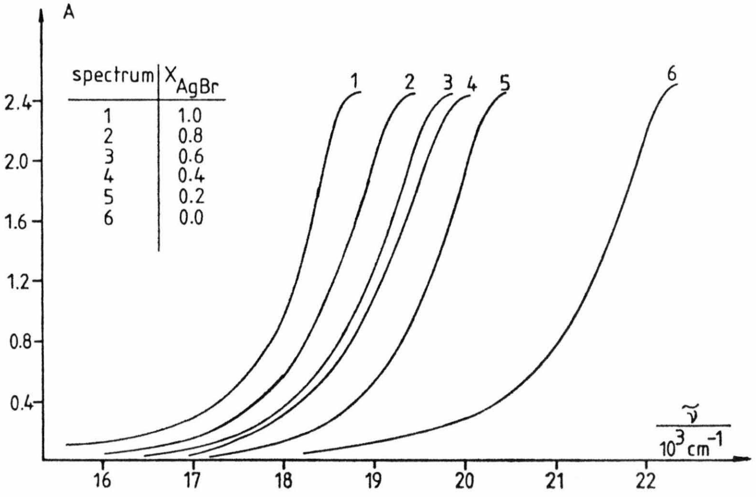


Fig. 7. Absorption edges of $AgCl_{1-x}Br_x$ melts.

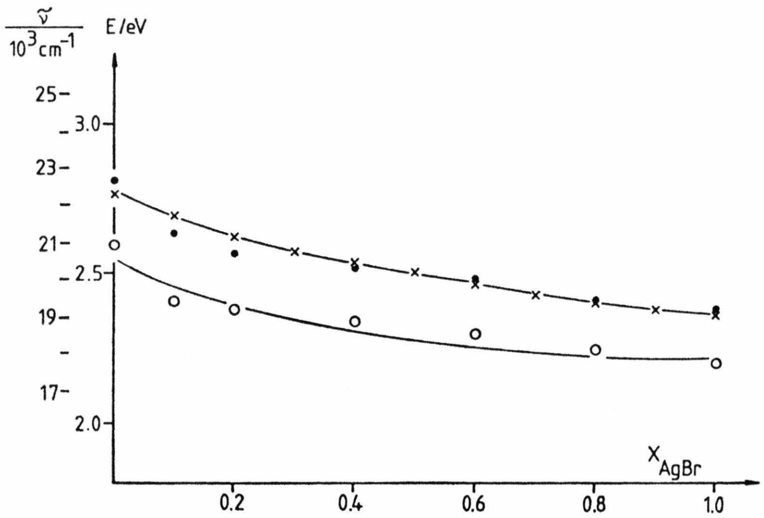


Fig. 8. Energy of constant absorption coefficient ($K = 100\ cm^{-1}$) for $AgCl_{1-x}Br_x$ mixtures (× : solids (from [9]) ● solids, this work, ○ melts).

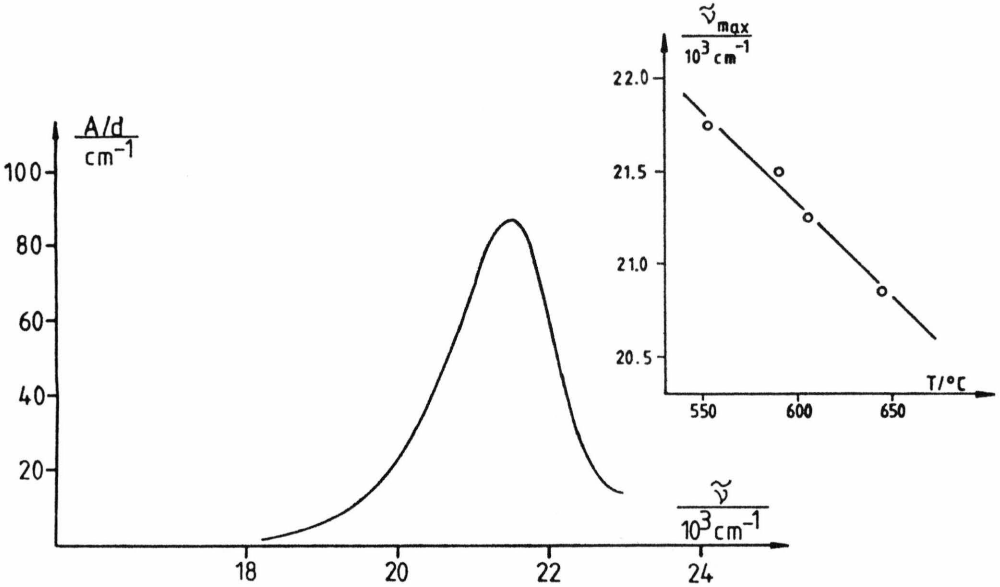


Fig. 9. Absorption spectra of an Ag-AgCl-melt; $T = 590\ °C$, $C_{Ag} = 0.03\ mol\ l^{-1}$, the insert shows the temperature dependence of the wave-number of the absorption maximum.

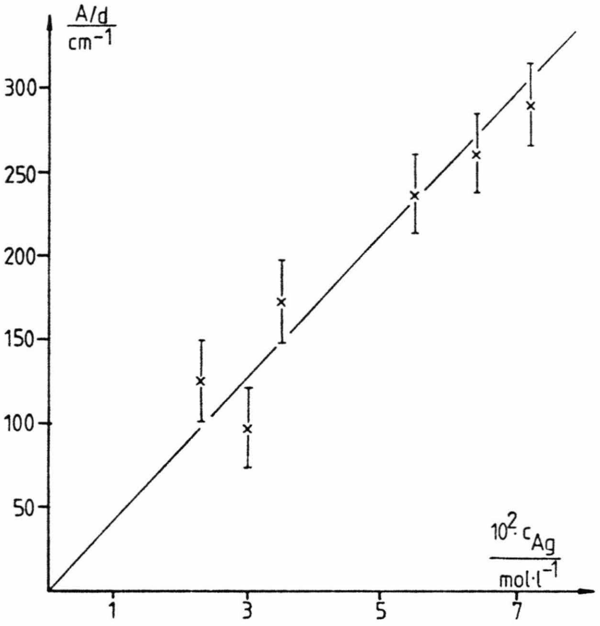


Fig. 10. Height of absorption maximum in AgCl melts as a function of the concentration of the dissolved silver.

4. Discussion

4.1. Electrical Conductivities

Electrical conductivities and their positive temperature coefficients for pure and silver saturated Ag(Cl, Br)-melts are of the order of magnitude of molten ionic conductors. It should be emphasized, that within the experimental errors there is no difference of conductivity between the silver saturated solutions and the pure melts.

The mole fraction of silver in the saturated melts is about 10^{-2}. Alkali metal concentrations of this order of magnitude in molten alkali halides result in an increase of conductivity by at least 10%. This comparison shows, that any model for the silver solutions which contains nearly free, or F-center-like electrons can be definitely ruled out.

It is known from measurements of the external transport numbers of AgCl melts that the silver ions move much more freely in the melt than the chlorine ions [10]. From Fig. 6 it is obvious that the apparent energy of activation has a minimum and a weak shoulder at 80 and 50 mol % AgBr, respectively. A similar but less striking dependence of the pre-exponential factor on the composition of the melt is also seen from Figure 6. At these compositions the solvation effects of the silver ions have extrema too [2].

4.2. Optical Spectra

From investigations of the optical spectra of the crystalline silver halides and their mixtures [9] it is known that the low energy tail of the absorption edge can be described by an equation, derived by Moser and Urbach [11],

$$K = K_0 \exp[-(\sigma/k_B T)(E_0 - E)] \qquad (2)$$

with K_0: empirical constant, σ: steepness parameter, E_0: energy gap of the indirect transition, and E: photon energy.

In the temperature range where our experiments were performed, the steepness parameter can be expected to be temperature independent [12]. Consequently, linear relationships should exist between $\ln K$ and the photon energy E, if the theory is applicable to the molten systems too. Indeed, straight lines are found, if the curves from Fig. 7 are plotted logarithmically versus the photon energy. For different temperatures the straight lines converge into the point $\ln K_0$ and E_0. Thus the energy gaps for the indirect transitions can be evaluated from our experiments as a function of the composition x of the molten systems $AgCl_{1-x}Br_x$. Figure 11 contains the results, together with literature data for the pure solids.

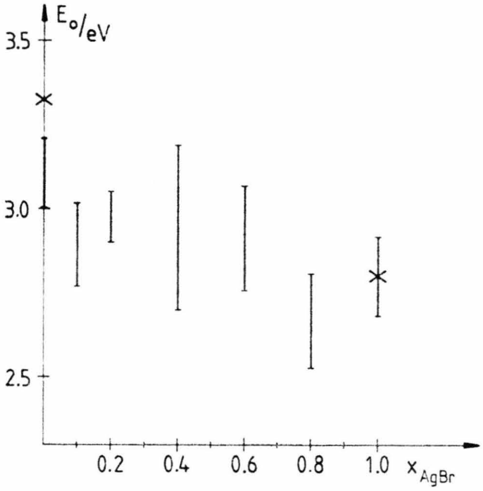


Fig. 11. Energy gap E_0 of $AgCl_{1-x}Br_x$ melts as a function of x at 750 K, × : Values from [12].

In the silver containing melts, the tail of the absorption edge is shifted to lower wave numbers. This observation can be explained in two different ways:

i) the dissolved silver acts as dopant which enhances the indirect transition,

ii) the dissolved silver forms a species, the electronic system of which is not coupled to the electronic system of the solvent. The additional absorption at the low energy tail ist due to direct transitions within the electronic system of the dissolved species.

Possibility i) can, for our cases, be ruled out by the following considerations: for impurity assisted indirect transitions, one may assume that either the band gap is decreased by an amount which is proportional to the mole fraction of the impurities, or that the steepness parameter in (2) would depend on the impurity concentration. In the latter case, the steepness of the ln K vs $(E_0 - E)$ curves should vary monotonously with y, the mole fraction of the dissolved silver. All our experiments show very clearly that there is no dependence of the steepness parameter on the concentration of the dissolved silver.

In the first case, from (2) one gets

$$K = K_0 \exp[-(\sigma/k_\mathrm{B} T)(E_0 - E - a y) \quad (3)$$

(a: empirical constant).

The ln K vs $(E_0 - E)$ plots should, for different y, give parallel straight lines. The values of these lines at $E_0 - E = 0$:

$$b = \ln K_0 - (\sigma/k_\mathrm{B} T) a y \quad (4)$$

should depend linearly on y.

In Fig. 12, this prediction is examined: There is no correlation of b with the silver concentration.

We therefore should prefer to interpret our results in terms of modell ii). In the frame of this model, the difference spectra between silver containing and pure melts can be interpreted as absorption bands of a dissolved species. The observed linearity between the hight of these bands and the silver concentration delivers further evidence for this model.

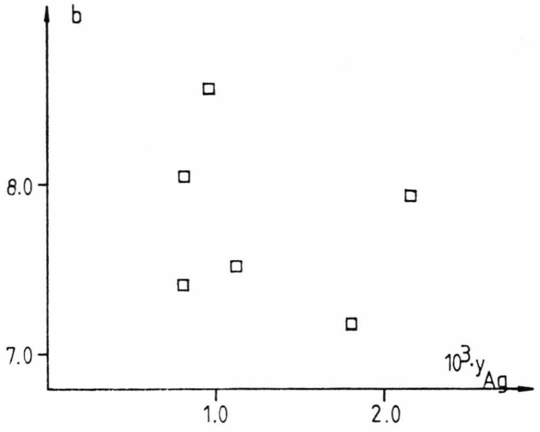


Fig. 12. Intercepts b from Eq. (3) as a function of y_Ag.

The wave numbers of the absorption edge of pure halides ($K = 1.5$) and of the band maxima of the silver solutions vs. the melt composition are shown in Figure 13. The band maxima of the solutions are always close to the absorption edges. The circles in Fig. 13 represent the wave numbers $\tilde{\nu}_{1.5}$ of the absorption edges while the squares give the position of the band maxima of the solutions. It is obvious from Fig. 13 that some melts have absorption maxima with wave numbers higher than the absorption edges. This is additional evidence for the existence of a new absorbing species, formed by the dissolved silver and which is entirely isolated from the electronic system of the surrounding medium.

From Fig. 13 it is seen that the wave numbers of absorption maxima do not vary monotonously with melt composition. Such a non-monotonous dependence had already been found for the enthalpy and entropy of solvation [2]. Strong negative enthalpies of solvation for melt compositions of 0

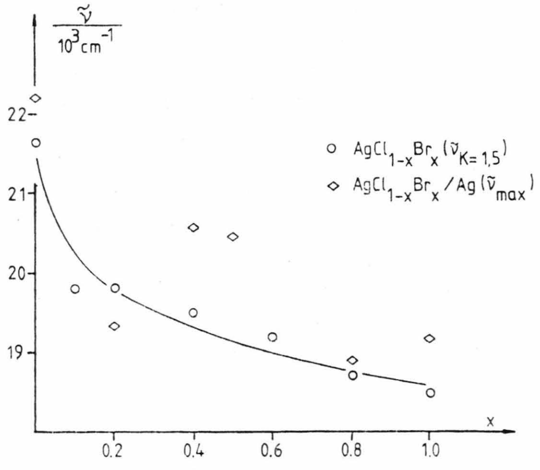


Fig. 13. Wave-numbers of absorption edges ($A = 1.5$) and band maxima in $AgCl_{1-x}Br_x$-melts as a function of x.

and 40 mol % AgBr correlate with high energies of excitation (high wave numbers of band maxima) while in melts with 20 mol % AgBr, where the enthalpy of solvation is weak, the wave numbers are lower.

Such a correlation between the wave number of the absorption maximum and the bond strength is known for many charge-transfer complexes [13]. The values of the wave numbers of the absorption bands and the corresponding half-widths are typical for such charge-transfer complexes. Statistical fluctuations in configurations and intra-molecular distances cause a broadening of these bands. These fluctuations are the larger the weaker the band energy. Therefore one should expect a decrease in half-width of the bands with increasing bond-energy. Unfortunately the bands partly overlap with the absorption edge. Therefore half-widths often could be only estimated and experimental data do not give the above mentioned correlation.

It was already mentioned [2] that the thermodynamic properties of the Ag/Ag Hal-systems are entirely different from those of the alkali-alkali halide systems. The physicochemical investigations reported above confirm this assumption. The process of dissolution of silver can not be described as a dissociation forming a silver cation and a nearly free electron. The formation of complexes with the formula $[Ag_{l+1}Cl_mBr_n]^{(l-m-n)+}$ seems more likely. This can be concluded from the dependence of the solvation effects on melt composition and from the missing increase of electrical conductivity. The absorption maxima are in the short-wavelength region of the spectrum whereas in alkali halides the excess electrons are loosely bound and can move freely [3, 4] and their absorption bands are in the red or near infrared region [6]. It is clear that the energy of formation of the above mentioned clusters may depend on the anion ratio. Also, if the interaction between the Ag° and the remainder of the cluster is of the charge transfer type, the optical properties of the solutions can be interpreted qualitatively.

Acknowledgement

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