Thermodynamics of Ag^0-Solvation in Molten Silver Halides, Doped with Metal Halides

Thomas Lieser and Konrad G. Weil
Institut für Physikalische Chemie, Technische Hochschule Darmstadt

Z. Naturforsch. **40 a,** 131 – 136 (1985); received December 2, 1984

Dedicated to Professor Dr. Alarich Weiss on the Occasion of his 60th Birthday

From the temperature dependence of the solubility of silver in its molten halides, the thermodynamic functions ΔH_{solv} and ΔS_{solv} are calculated. They depend strongly on the presence and concentration of mono- and divalent cations. A possible structure breaking effect of these ions is discussed.

1. Introduction

In a recent paper we reported on the dependence of the thermodynamic functions ΔH_{solv} and ΔS_{solv} of Ag^0 in molten $AgCl_{1-x}Br_x$ on the AgBr mole fraction x [1]. These functions vary non-monotonously with x. From UV-VIS spectra of the solution it could be tentatively concluded that Ag^0 is associated to complexes present in the melt via charge transfer interaction [2]. Therefore, the thermodynamic functions of solvation may be indicative for the activity of such complexes in the melt. The aim of the present paper is to show whether the thermodynamics of solvation of Ag^0 in its molten halides depends on the presence of ionic dopants. This would indicate that the structure of the melt can be influenced by these additives.

2. Experimental

In order to obtain the thermodynamic solvation functions of Ag^0 in molten silver halides, the thermodynamics of dissolution of metallic silver in these melts was derived from the temperature dependence of the solubility of the metal. The experimental procedure is described in detail in [1]. In order to obtain reliable values for the statistical errors, the van't-Hoff-equation

$$\ln y_{\text{Ag}} = -\frac{\Delta H_s}{RT} + \frac{\Delta S_s}{R} \qquad (1)$$

(y_{Ag}: saturation mole fraction of silver in the melt, ΔH_s and ΔS_s: enthalpy and entropy of dissolution) was solved by linear regression. The resulting standard deviations are given in the tables and, as error bars, in the figures of the present paper. The error limits given in [1] were only estimated. Therefore, some data were redetermined. Figure 1 shows as an example experimental points from [1] together with some additional points and the resulting regression line.

The functions ΔH_{solv} and ΔS_{solv}, which are associated with the process

Ag (in the ideal gas state $p = 1$ atm) →
Ag (solvated in the melt at standard concentration)

can be calculated with help of the sublimation functions:

$$\Delta H_{\text{solv}} = \Delta H_s - \Delta H_{\text{subl}}, \quad \Delta S_{\text{solv}} = \Delta S_s - \Delta S_{\text{subl}}.$$

These were taken from [3].

After purification of the melts, as described in [1], the desired concentration of the dopant was achieved by adding weighed amounts of the respective salts (p.a. from E. Merck, Darmstadt) to the melt. The following salts were used:

LiCl, KCl, CsCl, $ZnCl_2$, $CdCl_2$, $CaCl_2$, and $BaCl_2$.

3. Results

3.1. *Undoped melts $AgCl_{1-x}Br_x$*

All results concerning this system are collected in Table 1. Due to the limited temperature range in

---

Reprint requests to Prof. Konrad G. Weil, Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Petersenstraße 20, 6100 Darmstadt.

0340-4811 / 85 / 0200-0131 $ 01.30/0. – Please order a reprint rather than making your own copy.

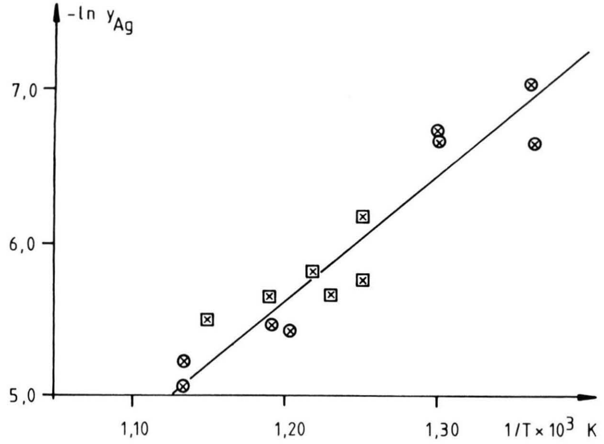


Fig. 1. Arrhenius plot, y_{Ag}: saturation mole fraction of silver in $AgCl_{0.28}Br_{0.72}$; circles: this work, squares: from [5].

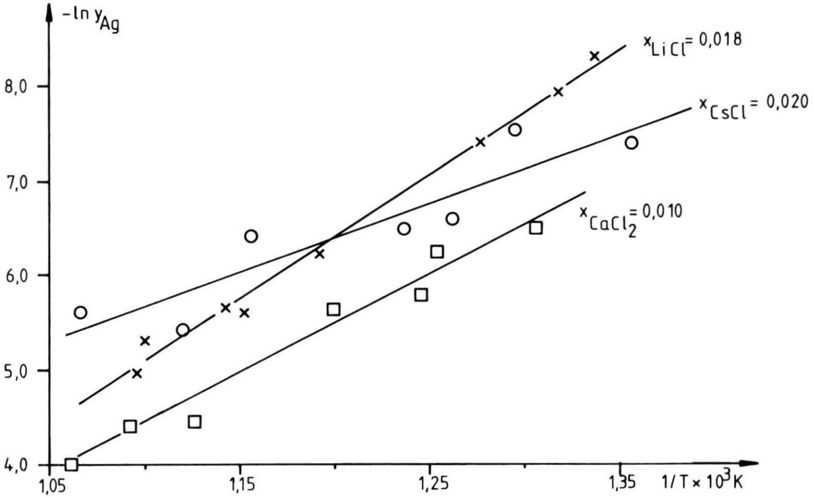


Fig. 2. Arrhenius plots, y_{Ag}: saturation mole fraction of silver in silver chloride, doped as indicated at the curves.

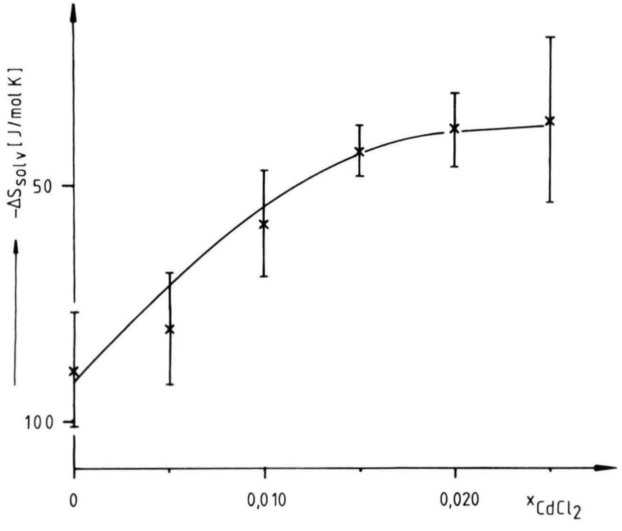


Fig. 3. Solvation entropy of silver in silver chloride as a function of the mole fraction x_{CdCl_2} of added dopant.

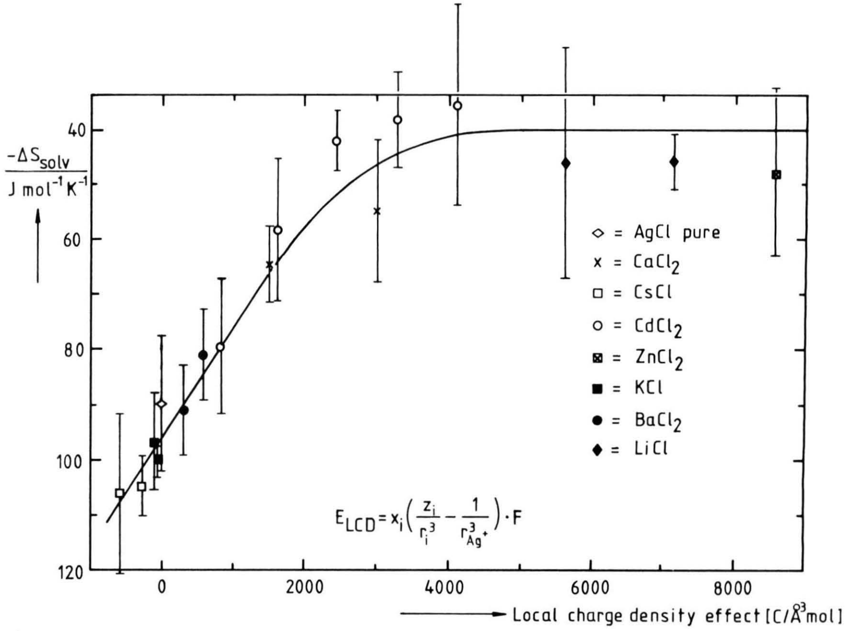


Fig. 4. Solvation entropy of silver in doped silver chloride as a function of the local charge density effect E_{LCD}.

Table 1. Thermodynamic functions of dissolution and solvation of silver in $AgCl_{1-x}Br_x$ melts.

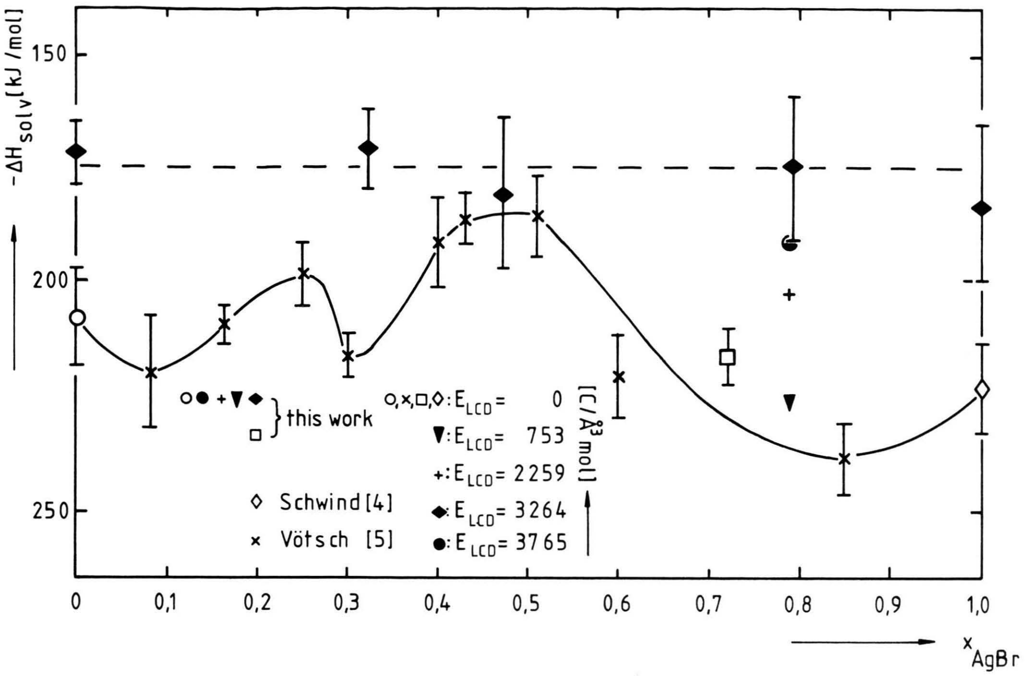
$AgCl_{1-x}Br_x$ x	ΔH_s (kJ/mol)	ΔS_s (J/mol K)	Standard Deviation in ΔH (kJ/mol)	Standard Deviation in ΔS (J/mol K)	$-\Delta H_{solv}$ (kJ/mol)	$-\Delta S_{solv}$ (J/mol k)
1.00	59	32	± 9	± 12	222	93
0.85	43	6	± 8	± 10	238	119
0.72	65	31	± 6	± 8	216	94
0.60	61	25	± 9	± 11	220	100
0.51	96	68	± 8	± 10	185	57
0.43	95	65	± 6	± 7	186	60
0.40	90	60	± 9	± 11	191	65
0.30	65	29	± 5	± 6	216	96
0.25	83	50	± 6	± 8	198	75
0.16	72	35	± 5	± 5	209	90
0.08	61	24	± 13	± 15	220	101
0.00	73	36	± 10	± 12	208	89

Table 2. Thermodynamic functions of dissolution and of solvation of silver in AgCl-melts doped with different cations.

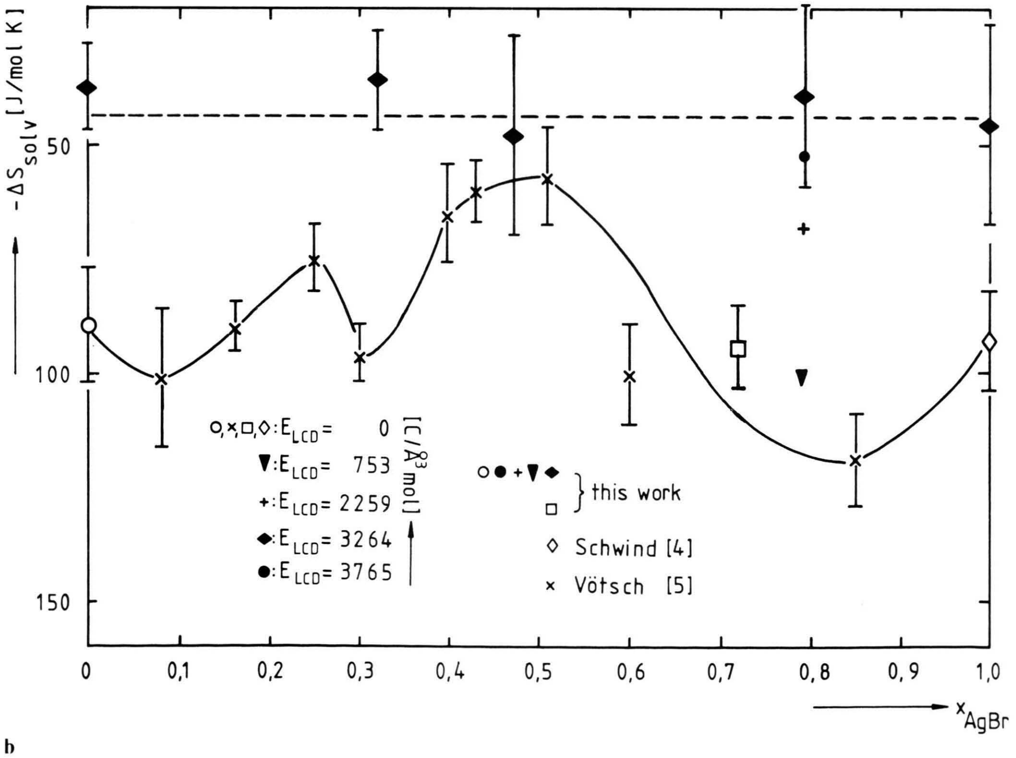
Dopant	x_{Dopant}	ΔH_s (kJ/mol)	ΔS_s (J/mol K)	Standard Deviation in ΔH (kJ/mol)	Standard Deviation in ΔS (J/mol K)	$-\Delta H_{solv}$ (kJ/mol)	$-\Delta S_{solv}$ (J/mol K)
$ZnCl_2$	0.020	98	76	± 13	± 16	183	49
LiCl	0.014	107	76	± 18	± 21	174	49
	0.018	110	78	± 4	± 5	171	47
$CdCl_2$	0.005	75	45	± 10	± 12	206	80
	0.010	94	66	± 11	± 13	187	59
	0.015	106	83	± 4	± 5	175	42
	0.020	109	87	± 7	± 9	172	38
	0.025	106	89	± 15	± 18	175	36
$CaCl_2$	0.010	88	60	± 6	± 7	193	65
	0.020	93	70	± 11	± 13	188	55
$BaCl_2$	0.010	68	30	± 7	± 8	213	95
	0.020	81	44	± 7	± 8	200	81
KCl	0.010	65	25	± 3	± 4	216	100
	0.020	67	29	± 7	± 9	214	96
CsCl	0.010	58	20	± 5	± 6	223	105
	0.020	61	19	± 12	± 14	220	106

Table 3. Thermodynamic functions of dissolution and of solvation of silver in $AgCl_{1-x}Br_x$-melts doped with different cations.

Dopant	x_{Dopant}	x_{AgBr} in $AgCl_{1-x}Br_x$	ΔH_s (kJ/mol)	ΔS_s (J/mol K)	Standard Deviation in ΔH (kJ/mol)	Standard Deviation in ΔS (J/mol K)	$-\Delta H_{solv}$ (kJ/mol)	$-\Delta S_{solv}$ (J/mol K)
$CdCl_2$	0.020	1.00	98	80	± 18	± 22	183	45
	0.020	0.79	106	86	± 16	± 20	175	39
	0.020	0.47	100	77	± 17	± 22	181	48
	0.020	0.32	110	89	± 9	± 11	171	36
	0.020	0.00	109	87	± 7	± 9	172	38
$CaCl_2$	0.005	0.79	55	25	± 5	± 6	226	100
	0.015	0.79	78	57	± 8	± 11	203	68
	0.024	0.79	89	73	± 8	± 10	192	52



a



b

Fig. 5. Solvation enthalpy (a) and solvation entropy (b) of silver in mixtures $AgCl_{1-x}Br_x$.

which the experiments can be performed, the standard deviations of the thermodynamic functions are relatively high. Nevertheless, the non-monotonous dependence of these functions on x can clearly be seen (cf. also Fig. 5).

3.2. *Doped melts*

The addition of small amounts (mole fraction $\leqq 0.02$) of different halides to molten silver chloride changes the solubility of silver and its temperature dependence markedly. Furthermore, as can be seen from Fig. 2, the influence is different for different cations.

The concentration dependence of the resulting solvation thermodynamics was studied with $CdCl_2$. Figure 3 shows that the entropy of solvation increases with increasing concentration of dopant. Saturation of this observation seems to occur at a mole fraction of dopant of about 0.02. The thermodynamic functions of solvation of silver in doped silver chloride melts, as far as they were determined in our experiments, are collected in Table 2. Some additional data were measured using mixed melts $AgCl_{1-x}Br_x$ as solvents. These results are presented in Table 3.

4. Discussion

The solvation entropy of Ag^0 in pure silver chloride is $-89\ \mathrm{J\,mol^{-1}\,K^{-1}}$. Addition of $CdCl_2$ leads to $\Delta S_{\mathrm{solv}} = -38\ \mathrm{J\,mol^{-1}\,K^{-1}}$ at $x_{\mathrm{CdCl_2}} = 0.02$. Other dopants have similar but smaller effects. Only the addition of KCl and LiCl makes the solvation entropy more negative than it is in the undoped melt. The solvation enthalpy is changed similarly. That means that the localization of the silver atoms under the influence of the dopants is smaller than in undoped melts. Salts which change the solvation properties of water in the same sense are called structure breakers [6].

From the high electrolytic conductivity of molten silver halides [8] it has to be concluded that on the time scale of this experiment the melt behaves like an ionic liquid. Neutron diffraction data [7], on the other hand, do not exclude the presence of structural entities like molecules or clusters, at least on the extremely fast time scale of the neutron diffraction experiment. The spectroscopic properties of Ag^0 in molten silver chloride [2] as well as the large negative entropy of solvation indicate strong localization of Ag^0 on these structural entities. If dopants convert the character of the melt from "partly covalent" to "more ionic", this structure breaking mechanism could explain the observed change of the solvation functions.

We tried to rationalize the specific effect of different ions as well as the concentration dependence. This was possible by introducing a local charge density effect E_{LCD}, defined as

$$E_{\mathrm{LCD}} = x_i \left(\frac{z_i}{r_i^3} - \frac{1}{r_{\mathrm{Ag^+}}^3} \right) F$$

with x_i: mole fraction of dopant i, z_i: its valency, and r_i: its ionic radius. F is Faraday's constant. Figure 4 clearly demonstrates that there is a unique relationship between this parameter and the change of the solvation entropy. Unfortunately we are not able to present any interpretation for this surprising result.

Nevertheless, the local charge density effect seems to be a quantitative measure for the amount of structure breaking or formation in a doped melt. This can also be seen from the properties of doped melts $AgCl_{1-x}Br_x$. In Fig. 5 a, b we present the results concerning the solvation enthalpy and entropy of silver in these melts as a function of x, which are also presented in Table 3. The figure contains the recalculated standard deviations. The latter are relatively high, but the peculiar non-monotonous shape of the curve which was already published in [1] can be recognized without doubt. In [1] we attributed this property of the x-dependence of ΔH_{solv} and ΔS_{solv} to the occurrence of complexes in the melt. These complexes were assumed to contain both anions Cl^- and Br^-. Also presented in Fig. 5 a, b are some points which were obtained with doped melts. These contained different amounts of $CdCl_2$ and $CaCl_2$, as specified in Table 3. The corresponding values of E_{LCD} are given in the figure. With increasing E_{LCD}, the minimum around $x = 0.8$ disappears gradually. When E_{LCD} exceeds $3000\ \mathrm{C\,Å^{-3}\,mol^{-1}}$, a dependence of ΔH_{solv} and ΔS_{solv} from x can no longer be detected.

Acknowledgements

Financial support by the Fonds der Chemischen Industrie is greatly acknowledged. Degussa, Hanau, kindly supported us with silver halides.

[1] E. Schuster, A. F. Schwind, R. Vötsch, and K. G. Weil, Z. Naturforsch. **34a,** 1203 (1979).
[2] A. F. Schwind, R. Vötsch, and K. G. Weil, Z. Naturforsch. **36a,** 354 (1981).
[3] I. Barin, O. Knacke, and O. Kubaschewski, in "Thermochemical Properties of Inorganic Substances, Suppl.", Springer-Verlag, Berlin 1977.
[4] A. F. Schwind, Dissertation Darmstadt.
[5] R. Vötsch, Dissertation Darmstadt.
[6] H. G. Hertz, Ber. Bunsenges. Phys. Chem. **67,** 311 (1963).
[7] J. Y. Derrien and J. Dupuy, Phys. Chem. Liq. **5,** 71 (1976).
[8] G. G. W. Greening and K. G. Weil, Z. Naturforsch. **39a,** 764 (1984).