Solubilities of Silver and Copper in Their Molten Halide Mixtures $AgCl_x Br_{1-x}$ and $CuCl_x Br_{1-x}$

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Z. Naturforsch. **34a**, 1203–1206 (1979); received August 24, 1979

Solubilities of silver and copper in their molten salt mixtures $AgCl_xBr_{1-x}$ and $CuCl_xBr_{1-x}$ were measured as a function of T and x. From the temperature dependence of the solubilities, the enthalpies and entropies of dissolution could be obtained as a function of x. Unexpectedly these functions vary nonmonotonously with x. The enthalpies and entropies of solution were calculated from the experimental values, using literature data for the sublimation functions. They are found to be linearly correlated. The results are tentatively discussed under consideration of the covalent nature of the melt.

1. Introduction

Previous investigations on molten salts as solvents for non volatile substances are mostly concerned with solutions of metals in their molten halides. Most of these investigations deal with the alkali halides which show remarkable solubilities for their metals [1, 2]. In some cases one finds complete miscibility between the molten salts and their molten metals. These systems are of special interest for their continuous transition from salt-like to metallic behaviour [3, 4].

There is little knowledge, on the other hand, about the solubilities of the Ib-metals, silver and copper, in their molten halides. Corbett and Winbush [5] reported the equilibrium mole fraction of silver in molten silver chloride at 490 °C to be $y_{\mathrm{Ag}} = 3 \cdot 10^{-4}$. A more detailed study on the equilibria in the systems Ag/AgX (X = Cl, Br and I) including the temperature dependence appeared in 1971 [6].

The solubilities were found to be small and the enthalpies of solution, obtained from van't Hoff-plots, varied only slightly from solvent to solvent.

In the alkali/alkali halide systems, the properties of the solutions are well represented by the F-center model. In this model the dissolved metal dissociates, forming a cation which becomes an ordinary member of the mixture, and an electron, located at an anion vacancy. In the systems Ib metal/Ib halide the situation is entirely different. The solid salts crystallise in the NaCl type with Frenkel disorder, so that no anion vacancies are present in the solid. Interstitial silver ions are, at room temperature, very effective electron traps. At elevated temperatures, these traps may dissociate. However, in order to establish a stable state for the molten metal, there should be a bound state either for the electron or for the atom.

One has to assume that covalent interactions between the metal and the anions have to come into play. In this case, the anionic surroundings of the dissolved species should be of importance for the binding energy and hence for the thermodynamic functions of dissolution. In this paper we shall report on measurements of these thermodynamic functions using mixed salts $AgCl_xBr_{1-x}$ and $CuCl_xBr_{1-x}$ as solvent.

2. Experimental

2.1. *Solubility of Silver in the $AgCl_xBr_{1-x}$ System*

The silver halides were purchased from Degussa. In order to obtain a desired fraction x, calculated masses of the pure salts were weighed into a quartz vessel of 5 cm height and 2 cm diameter. The total mass always ranged from 20 to 25 g. The salt was molten in an electric furnace. For the temperature measurement, a Ni/NiCr thermocouple, which was protected by a quartz tubing, was inserted into the melt. The thermovoltage was recorded with a compensating recorder from Metrawatt. During an experiment of about 24 h duration, the temperature was constant to within ±2 °C. In order to oxidise any photolytically formed silver, a bromine-containing stream of argon was bubbled through the melt

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for at least 2 h. Then the remaining bromine was removed by pure argon.

Before adding the silver to the melt, it was washed with diluted KCN and then with distilled water, dried and carefully weighed. It had the shape of small rods and was of 99.99% purity. After at least 24 h the melt was removed. The silver was again cleaned with aqueous KCN, rinsed with water and, after careful drying, weighed. From the mass difference and the known amount of substance of the melt the mole fraction of the silver could be calculated.

2.2. *Solubility of Copper in the $CuCl_xBr_{1-x}$ System*

The pure salts CuCl and CuBr were prepared according to Keller and Wycoff [7] by reduction of $CuCl_2 \cdot 2H_2O$ or $CuBr_2 \cdot 2H_2O$ (both p.a.-grade from Merck) with Na_2SO_3 (p.a.-grade from Merck) under argon atmosphere. In order to avoid oxidation by air, mixtures of known composition together with copper of known mass were heated in sealed quartz ampoules. The temperature was kept constant for about 30 h. The final procedure was the same as with silver.

3. Results

3.1. *Silver*

The equilibrium mole fraction y_{Ag} in molten mixtures $AgCl_xBr_{1-x}$ was determined as function of T and x. From the integrated van't Hoff equation

$$\ln y_{Ag} = -\Delta H_s/RT + \Delta S_s/R$$

(ΔH_s, ΔS_s: enthalpy and entropy of dissolution), the thermodynamic functions can be obtained by plotting $\ln y_{Ag}$ vs. $1/T$ at constant x. Figure 1 shows some typical results. The figure shows straight lines, indicating that ΔH_s and ΔS_s are constant for a given x. The slope of these lines as well as the intercepts with the ordinate are strongly dependent on x.

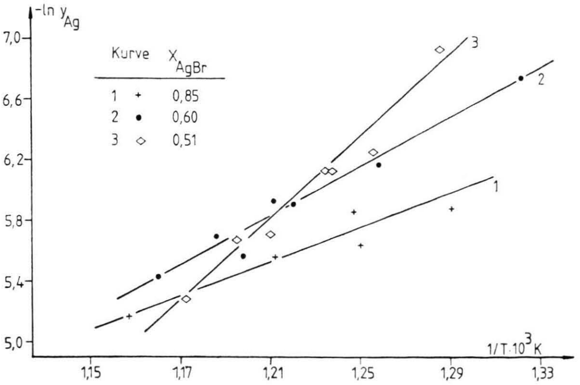

Fig. 1. Logarithmic plot of the equilibrium mole fraction of silver in melts of different composition vs. reciprocal temperature.

Enthalpies and entropies of dissolution were obtained from the experimental data by a least-squares method. They are listed in Table 1. Figure 2 gives a graphic representation of the dependency

Table 1. Thermodynamic functions of dissolution and of solvation of silver in the mixed melts.

x	ΔH [kJ mol^{-1}]	ΔS [J mol^{-1} K^{-1}]	$-\Delta H_{solv}$ [kJ mol^{-1}]	$-\Delta S_{solv}$ [J mol^{-1} K^{-1}]
0,00*	41	2	241	123
0,08	60	23	221	102
0,16	73	35	208	90
0,19	86	62	195	63
0,25	85	53	196	72
0,30	67	30	214	95
0,34	66	39	215	86
0,40	84	53	197	72
0,43	109	82	172	43
0,46	101	82	180	43
0,51	97	69	184	57
0,56	83	62	198	63
0,60	59	23	222	102
0,65	29	− 9	259	134
0,72	34	− 6	247	131
0,79	23	−19	258	144
0,85	42	5	239	120
0,95	55	29	226	97
1,00*	61	35	220	91

* nach [6].

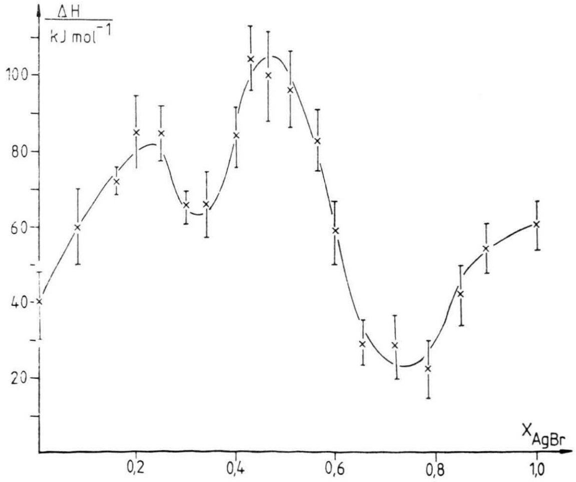

Fig. 2. Enthalpy of dissolution of silver in the mixed melts vs. the composition of the melt.

of the enthalpy of dissolution on the composition of the molten salt.

3.2. Copper

The results obtained with copper in equilibrium with molten mixtures of CuCl and CuBr resemble closely those reported in the preceding section. Again the thermodynamic functions of dissolution are constant for a given x. They are collected in Table 2. Figure 3 likewise shows the strong non-monotonous dependency of the enthalpy of dissolution on the composition of the melt.

4. Discussion

In order to obtain figures that are representative for the interaction between the solvent and the dissolved species from our experimental results, one has to calculate the thermodynamic functions for the process

Metal (ideal gas at 1 bar) → dissolved species.

These quantities, the enthalpy of solvation and the entropy of solvation, are connected with the experimental enthalpies and entropies of dissolution by the equations

$$\Delta H_{\mathrm{solv}} = \Delta H_{\mathrm{s}} - \Delta H_{\mathrm{subl}}\,,$$
$$\Delta S_{\mathrm{solv}} = \Delta S_{\mathrm{s}} - \Delta S_{\mathrm{subl}}\,.$$

The sublimation functions can be calculated from literature data [8]. Table 1 and 2 contain the results. For convenience the same values are plotted in Figs. 5 and 6 vs. the composition of the melt. It is obvious from these figures that the solvation functions are strongly negative and depend on the composition of the melt in a non-monotonous manner. This leads to the conclusion that the dissolved species are strongly solvated and that the composition of the solvation shell and also the binding energy between central species and solvation shell depends on the overall composition of the melt. In this case, the gain in order around the dissolved species and therefore the solvation entropy should depend on the binding energy, represented by the

Table 2. Thermodynamic functions of dissolution and of solvation of copper in the mixed melts.

x	ΔH [kJ mol^{-1}]	ΔS [J mol^{-1}K^{-1}]	$-\Delta H_{\mathrm{solv}}$ [kJ mol^{-1}]	$-\Delta S_{\mathrm{solv}}$ [J mol^{-1} K^{-1}]
0	73	31	257	93
0,1	43	4	284	116
0,2	53	17	276	107
0,3	60	25	270	100
0,4	77	43	252	81
0,5	90	57	240	67
0,6	90	64	240	60
0,7	80	51	250	73
0,8	51	18	278	104
0,9	58	27	272	97
1,0	61	34	269	89

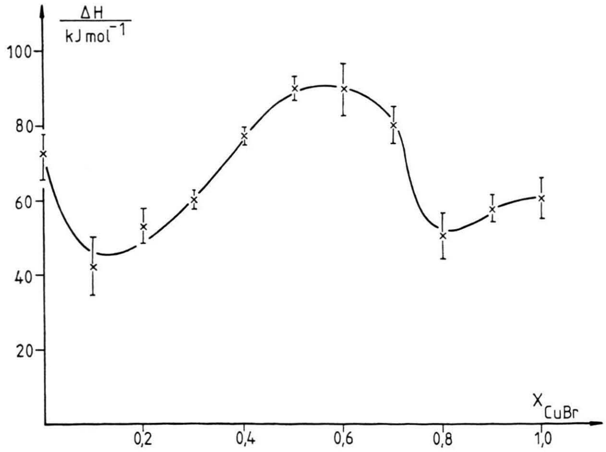

Fig. 3. Enthalpy of dissolution of copper in the mixed melts vs. the composition of the melt.

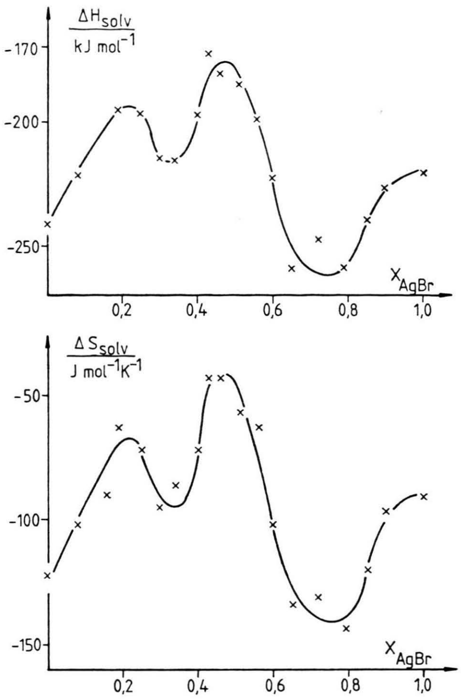

Fig. 4. Enthalpy and entropy of solvation of silver in the mixed melts vs. the composition of the melt.

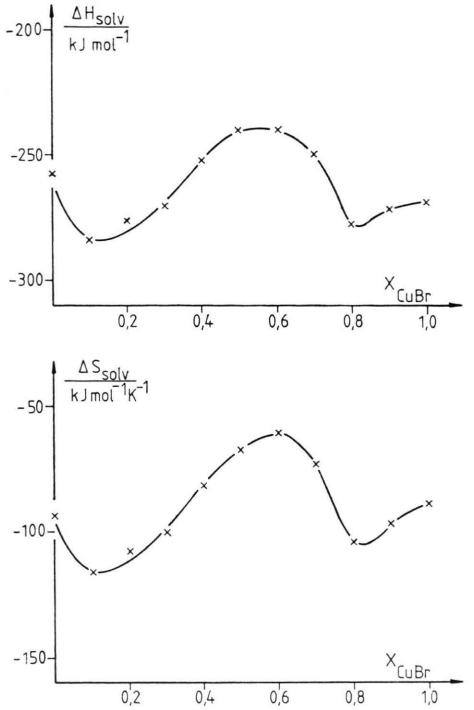

Fig. 5. Enthalpy and entropy of solvation of copper in the mixed melts vs. the composition of the melt.

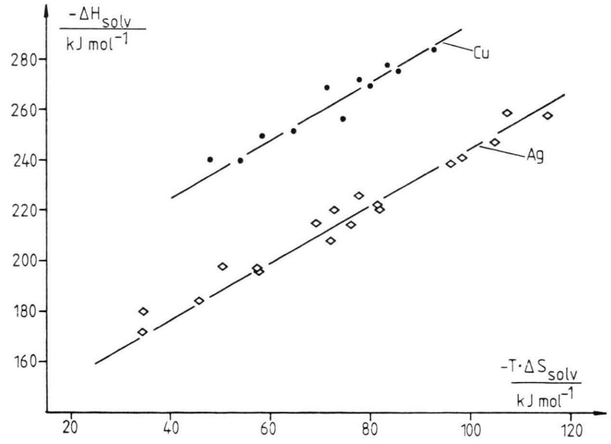

Fig. 6. Relationship between the solvation functions of silver and copper.

enthalpy of solution. The validity of this assumption can be seen from Fig. 6, a plot of ΔH_{solv} vs. $T \Delta S_{\text{solv}}$. The observed linear relationship between the solvation functions leads to the conclusion that the solubility of the metals in the mixed solvents should be nearly independent of x, the composition of the melt.

The following conclusions can be drawn from the reported results: the properties of the systems Ag/AgX and Cu/CuX are entirely different from those of the alkali/alkali halide systems. This is due to the different nature of the melts. Alkalihalide melts are purely ionic melts which contain vacancies in high concentration. The relative change of volume at melting of all alkalihalides is about 0.2 to 0.3 while the relative distance between next neighbours decreases by about 5% [9]. For silver chloride the relative volume change is only 8%, but the decrease in relative distance between next neighbours amounts to 12%. The property of the melt can therefore be said to be mainly governed by the covalent interactions between the metal atoms and the halogen. It seems reasonable, under these conditions, that the interaction which stabilises the dissolved species in these systems is also covalent. This means that the dissolved species are to be described as clusters with formulas such as $Ag_l Cl_m Br_n{}^{(m+n+1-l)-}$. The existence of clusters in pure AgCl melts is confirmed by neutron diffraction experiments [10].

It does not seem possible to obtain more detailed information on the state of the metal solutions in the system Ag/AgX and Cu/CuX by purely thermodynamic methods. In order to characterise the state of these systems further, different physical properties of them must be studied. In the following paper we will report on such experiments.

Acknowledgements

Financial support by the Fonds der Chemischen Industrie is greatly appreciated.

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