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Thermodynamics and Equilibrium Phase Diagrams of the Zinc Halide + Silver Halide Systems

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Phase equilibrium diagrams for the systems zinc chloride + silver chloride and zinc bromide + silver bromide were determined by differential scanning calorimetry and X-ray diffraction methods, using high-purity materials and a glovebox for sample preparation. Both equilibrium phase diagrams are of the simple eutectic type. The eutectic points are at 504 K, 53.5 mol % AgCl, and 551 K, 59.4 mol % AgBr, respectively. On the basis of the determined liquidus temperatures, the thermodynamic activities of components in liquid solutions $ZnCl_2$ + AgCl and $ZnBr_2$ + AgBr as well as the integral molar free enthalpies of mixing and the integral molar excess free enthalpies were calculated and discussed in terms of structure of molten salt mixtures.

Introduction

Studies of phase equilibria in the systems involving zinc chloride and zinc bromide are confronted with difficulties because these salts reveal a glass-forming tendency[1,2] and are extremely hygroscopic.[3,4] Many of the corresponding phase diagrams are still not known. On the other hand, in recent years there has been an increasing interest in zinc halide based glasses.[5,6] Establishing phase diagrams can therefore prove extremely relevant for further studies.

The aim of our work was to investigate the phase equilibria in the systems zinc chloride + silver chloride and zinc bromide + silver bromide and to establish phase diagrams for these systems as well as to determine thermodynamic activities and free enthalpies of mixing of the components in molten salt solutions. To our knowledge, no phase-diagram data for the $ZnBr_2$ + AgBr system is available. For the $ZnCl_2$ + AgCl system, the only original work is that of Glistenko and Artemova.[7] The phase diagram was reported to be a simple eutectic on the basis of the “visual-polythermic” method. Only effects of the primary crystallization were observed. Results for nine $ZnCl_2$ + AgCl mixtures were shown. The eutectic point, estimated later from these data, e.g., by Palkin and Shchirova[8] or by Voskresenskaya,[9] was given to be at 521 K and 57 mol % AgCl (in original text: 60 equivalent % $ZnCl_2$) or at 521 K and 52 mol % AgCl, respectively.

Experimental Section

In this work, all handling of samples involving zinc halides was undertaken in a glovebox. The phase diagrams for the systems $ZnCl_2$ + AgCl and $ZnBr_2$ + AgBr have been determined mainly by differential scanning calorimetry (DSC). An additional method employed was X-ray diffraction.

Salts of high purity were used. Silver halides AgCl and AgBr were precipitated from a dilute aqueous solution of $AgNO_3$ (reagent grade) with a solution of hydrochloric or hydrobromic acid, respectively. The precipitate was carefully washed, dried, and melted in an electric furnace. Special care was taken to avoid exposition to light. Zinc halides were commercially available products, $ZnCl_2$ (99.99%, Aldrich) and $ZnBr_2$ (99.999%, Aldrich), delivered in sealed glass ampules.

Mixtures for DSC and X-ray diffraction experiments were prepared in a Labmaster 130 MBraun glovebox, filled with dry helium gas (<1 ppm O_2, <4 ppm H_2O). Appropriate quantities of silver halide and zinc halide were introduced into the silica ampules, next sealed under a vacuum.

Phase-equilibrium studies were performed with a Mettler Toledo DSC 25 measuring cell, equipped with a heat flow sensor and joined via interface TA Controller TC 15 to a computer. The updated version of the basic software $STAR^e$ 6.0 was used.

All the samples with the mixtures $ZnCl_2$ + AgCl and $ZnBr_2$ + AgBr were heated with a rate of 5 K min^{-1} in the temperature range of 323 K to 773 K and 323 K to 723 K, respectively. Other heating or cooling rates (0.5, 1, 2, 10) K min^{-1} were also used when needed. The accuracy of the temperature and the composition determination was on the average 1 K and 0.1 mol %, respectively. The compositions of the eutectic points were determined by extrapolation (liquidus curves and Tamman triangle methods) with an accuracy of ±0.5 mol %.

X-ray powder patterns were obtained with a DRON-3-type diffractometer at room temperature with Co $K\alpha$ radiation. Samples for X-ray diffraction experiments, prepared in the glovebox, were protected against atmospheric moisture during exposition.

Results

Equilibrium Phase Diagrams. Our results show that both systems, $ZnCl_2$ + AgCl and $ZnBr_2$ + AgBr (Figure 1), are of the eutectic type. Melting points of the pure components are 587 K, 728 K, 675 K, and 693 K for $ZnCl_2$, AgCl, $ZnBr_2$, and AgBr, respectively. Eutectic points are at 504 ± 2 K, 53.5 mol % AgCl, and 551 ± 2 K, 59.4 mol %, AgBr, respectively.

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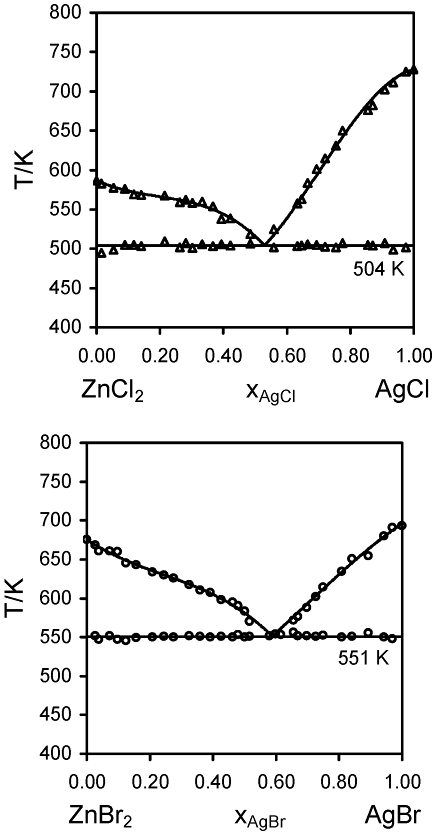

Figure 1. Phase equilibrium diagrams of the systems $ZnCl_2$ + AgCl and $ZnBr_2$ + AgBr.

Thermal effects corresponding to the eutectic reaction were noticeable on DSC thermograms for all the mixtures examined. Examples of DSC curves showing both eutectic and liquidus events are given in Figure 2. Tamman constructions confirmed that there was no reciprocal miscibility in the solid state. X-ray diffractograms showed pure components to be the only phases coexisting at room temperature in both systems.

Table 1. Enthalpy of Fusion and Molar Heat Capacity of Silver and Zinc Halides

	$\Delta_{fus}H$/ kJ mol^{-1}	ref	C_p/J·mol^{-1}·K^{-1} = $A + B(T/K) + C(T/K)^{-2}$				ref
			phase	A	B	C	
AgCl	13.22	11	liquid	57.3			11
			solid	41.30	0.03323		11
AgBr	9.14	12	liquid	67.722			13
			solid	−63.839	0.21402	5896762	13
$ZnCl_2$	16.1	14	liquid	100.83			14
			solid	59.83	0.03766		14
$ZnBr_2$	15.6	14	liquid	113.8			14
			solid	52.72	0.04351		14

Thermodynamics of Molten Salt Solutions. Thermodynamic activities of components as well as molar free enthalpies of mixing for liquid solutions were calculated based on liquidus temperatures for both systems in the entire range of compositions.

In the equilibrium range between the pure solid component 1 and the molten salt solution, the thermodynamic activity a_1^l of component 1 in the liquid solution is[10]

$$\ln a_1^l = \frac{\Delta_{fus}H_1}{R}\left(\frac{1}{T_1^f} - \frac{1}{T}\right) + \frac{\Delta A_{l,s}}{R}\left(\frac{T_1^f}{T} - 1 + \ln\frac{T}{T_1^f}\right) + \frac{\Delta B_{l,s}}{2RT}(T_1^f - T)^2 + \frac{\Delta C_{l,s}}{2R}\left(\frac{1}{T_1^f} - \frac{1}{T}\right)^2 \quad (1)$$

where $\Delta_{fus}H_1$ is the enthalpy of fusion of component 1, R the gas constant, T_1^f the melting point of component 1, and T is the liquidus temperature. $\Delta A_{l,s}$, $\Delta B_{l,s}$, and $\Delta C_{l,s}$ are coefficients in the following equation, describing the difference $(C_p^l - C_p^s)$ of component 1 molar heat capacities in the liquid and solid states as a function of temperature

$$C_p^l - C_p^s = \Delta A_{l,s} + \Delta B_{l,s}T + \Delta C_{l,s}T^{-2} \quad (2)$$

The partial molar free enthalpy of mixing G_1 and partial molar excess free enthalpy G_1^E of the component are related to the thermodynamic activity a_1 by the following

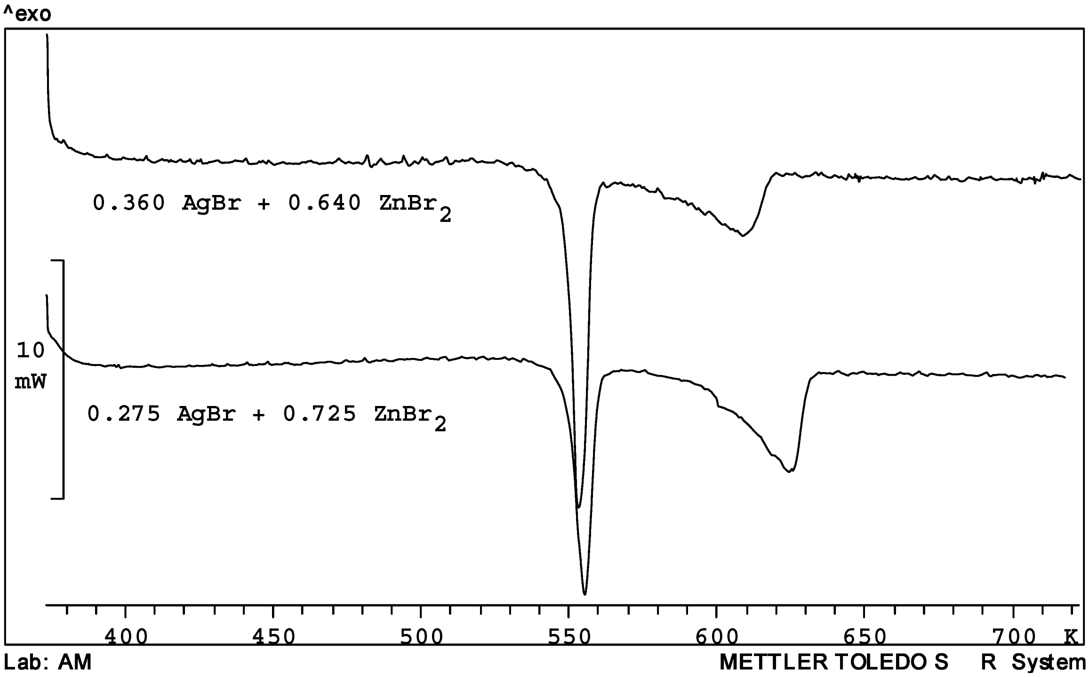

Figure 2. Examples of DSC thermograms performed at a heating rate of 5 K min^{-1} and showing both eutectic and liquidus event.

Table 2. Thermodynamic Properties of Liquid Solutions $ZnCl_2$ (1) + AgCl (2)

x_2	T/K	a_1	a_2	G_1/kJ mol^{-1}	G_2/kJ mol^{-1}	G_1^E/kJ mol^{-1}	G_2^E/kJ mol^{-1}	G^M/kJ mol^{-1}	G^E/kJ mol^{-1}
0.000	587	1.000	0.000	0.000		0.000		0.000	0.000
0.015	583	0.976	0.027	−0.117	−17.434	−0.044	2.912	−0.377	0.001
0.053	578	0.949	0.110	−0.252	−10.610	0.009	3.499	−0.801	0.194
0.089	576	0.940	0.128	−0.298	−9.835	0.149	1.750	−1.147	0.291
0.118	569	0.904	0.181	−0.480	−8.088	0.114	2.025	−1.378	0.340
0.142	568	0.899	0.187	−0.501	−7.920	0.222	1.304	−1.555	0.376
0.214	567	0.894	0.195	−0.531	−7.719	0.605	−0.447	−2.069	0.380
0.263	559	0.852	0.227	−0.742	−6.895	0.677	−0.685	−2.360	0.319
0.281	562	0.862	0.220	−0.692	−7.073	0.847	−1.140	−2.485	0.289
0.303	559	0.849	0.229	−0.761	−6.852	0.916	−1.307	−2.606	0.242
0.332	560	0.853	0.226	−0.737	−6.917	1.140	−1.788	−2.789	0.168
0.367	554	0.824	0.242	−0.892	−6.539	1.213	−1.926	−2.964	0.061
0.394	538	0.746	0.284	−1.307	−5.630	0.931	−1.468	−3.011	−0.014
0.421	538	0.749	0.282	−1.292	−5.660	1.153	−1.790	−3.131	−0.086
0.484	518	0.660	0.328	−1.792	−4.807	1.058	−1.680	−3.251	−0.267
0.558	525	0.513	0.411	−2.915	−3.882	0.645	−1.338	−3.454	−0.461
0.633	558	0.392	0.498	−4.338	−3.233	0.309	−1.113	−3.638	−0.591
0.645	563	0.374	0.512	−4.596	−3.131	0.250	−1.079	−3.651	−0.607
0.665	584	0.309	0.571	−5.698	−2.722	−0.390	−0.742	−3.719	−0.624
0.693	601	0.262	0.621	−6.700	−2.383	−0.796	−0.550	−3.708	−0.625
0.721	615	0.227	0.661	−7.578	−2.117	−1.050	−0.445	−3.641	−0.613
0.756	631	0.189	0.708	−8.744	−1.809	−1.342	−0.341	−3.501	−0.585
0.777	650	0.149	0.766	−10.313	−1.444	−2.199	−0.080	−3.422	−0.552
0.856	676	0.097	0.843	−13.093	−0.959	−2.198	−0.084	−2.706	−0.389
0.870	682	0.086	0.860	−13.874	−0.856	−2.311	−0.067	−2.548	−0.358
0.909	702	0.051	0.920	−17.363	−0.485	−3.380	0.072	−2.021	−0.242
0.935	711	0.036	0.948	−19.628	−0.316	−3.473	0.082	−1.571	−0.150
0.975	725	0.016	0.991	−24.843	−0.055	−2.602	0.098	−0.674	0.031
1.000	728	0.000	1.000		0.000		0.000	0.000	0.000

Table 3. Thermodynamic Properties of Liquid Solutions $ZnBr_2$ (1) + AgBr (2)

x_2	T/K	a_1	a_2	G_1/kJ mol^{-1}	G_2/kJ mol^{-1}	G_1^E/kJ mol^{-1}	G_2^E/kJ mol^{-1}	G^M/kJ mol^{-1}	G^E/kJ mol^{-1}
0.000	675	1.000	0.000	0.000		0.000		0.000	0.000
0.027	668	0.971	0.050	−0.166	−16.683	−0.014	3.383	−0.612	0.078
0.039	661	0.940	0.128	−0.342	−11.293	−0.123	6.523	−0.769	0.136
0.073	661	0.942	0.137	−0.328	−10.930	0.089	3.455	−1.102	0.334
0.097	660	0.939	0.143	−0.346	−10.691	0.214	2.117	−1.350	0.399
0.124	645	0.879	0.245	−0.691	−7.542	0.019	3.652	−1.541	0.469
0.157	643	0.872	0.258	−0.731	−7.235	0.182	2.666	−1.752	0.572
0.208	634	0.836	0.316	−0.944	−6.066	0.284	2.206	−2.010	0.684
0.246	630	0.822	0.336	−1.028	−5.703	0.451	1.640	−2.178	0.743
0.275	626	0.807	0.356	−1.115	−5.381	0.558	1.336	−2.288	0.772
0.326	618	0.777	0.391	−1.294	−4.827	0.732	0.929	−2.445	0.796
0.360	610	0.751	0.420	−1.453	−4.407	0.811	0.776	−2.516	0.799
0.393	608	0.742	0.429	−1.508	−4.276	1.014	0.442	−2.596	0.789
0.426	598	0.710	0.460	−1.705	−3.865	1.056	0.380	−2.625	0.768
0.462	595	0.698	0.470	−1.776	−3.731	1.290	0.088	−2.680	0.734
0.479	591	0.684	0.483	−1.868	−3.574	1.333	0.039	−2.685	0.713
0.501	583	0.659	0.504	−2.023	−3.325	1.346	0.025	−2.675	0.684
0.516	570	0.618	0.539	−2.279	−2.935	1.162	0.203	−2.617	0.667
0.656	572	0.463	0.655	−3.662	−2.011	1.410	−0.008	−2.579	0.480
0.669	577	0.441	0.671	−3.926	−1.916	1.374	0.011	−2.581	0.462
0.699	588	0.393	0.705	−4.562	−1.706	1.303	0.044	−2.566	0.423
0.726	602	0.336	0.749	−5.453	−1.445	1.023	0.157	−2.543	0.394
0.749	614	0.290	0.788	−6.315	−1.220	0.745	0.256	−2.498	0.379
0.808	634	0.224	0.846	−7.900	−0.881	0.801	0.243	−2.228	0.350
0.841	651	0.172	0.894	−9.540	−0.609	0.414	0.328	−2.029	0.342
0.894	655	0.157	0.904	−10.078	−0.552	2.140	0.058	−1.562	0.279
0.943	680	0.073	0.969	−14.836	−0.178	1.367	0.154	−1.013	0.223
0.970	691	0.043	0.994	−18.018	−0.034	2.124	0.140	−0.574	0.200
1.000	693	0.000	1.000		0.000		0.000	0.000	0.000

equation

$$G_1 = RT \ln a_1 = RT \ln x_1 + G_1^E \tag{3}$$

A similar equation is used for the thermodynamic activity of component 2 in the liquid solution, in the equilibrium range between the pure solid component 2, and the molten salt solution. The Gibbs−Duhem equation is then applied to calculate the partial molar excess free enthalpies of components over the entire range of compositions.

The integral molar free enthalpies of mixing G^M and integral molar excess free enthalpies G^E are given by

$$G^M = x_1G_1 + x_2G_2 \tag{4}$$

$$G^E = x_1G_1^E + x_2G_2^E \tag{5}$$

To apply the above equations, enthalpies of fusion of the components, and coefficients in the equation mentioned beforehand, describing the difference between molar heat capacities of component in the liquid and solid states is

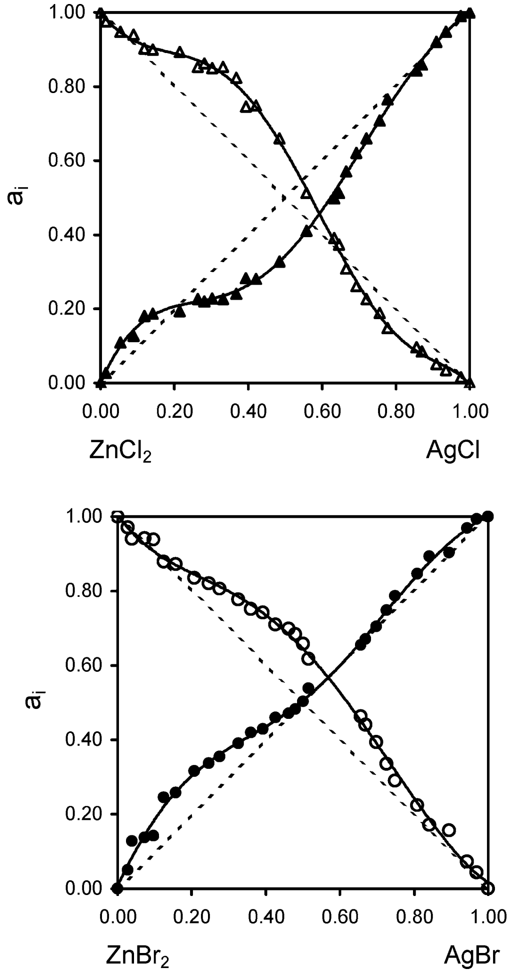

Figure 3. Thermodynamic activities in the molten systems $ZnCl_2$ + AgCl and $ZnBr_2$ + AgBr.

necessary. Appropriate values[11−14] are gathered in Table 1.

Calculated thermodynamic quantities, thermodynamic activities of components, partial molar free enthalpies of mixing, partial molar excess free enthalpies in liquid solutions $ZnCl_2$ + AgCl and $ZnBr_2$ + AgBr in the whole range of compositions, as well as the integral molar free enthalpies of mixing and the integral molar excess free enthalpies, for both systems are listed in Tables 2 and 3, respectively.

Thermodynamic activities of components vs composition in liquid solutions $ZnCl_2$ + AgCl and $ZnBr_2$ + AgBr are plotted in Figure 3. The integral molar free enthalpies of mixing and the integral molar excess free enthalpies for both systems are shown in Figure 4.

Discussion

Deviations from the ideal solution behavior are positive for solutions rich in zinc halide. Freezing-point depressions of the pure zinc halides caused by respective silver halides are not considerable. Liquidus lines corresponding to crystallization of $ZnCl_2$ or $ZnBr_2$ (Figure 1) do not fall down steeply and extend beyond 50 mol % of AgCl or AgBr, respectively. Consequently, in both systems $ZnCl_2$ + AgCl and $ZnBr_2$ + AgBr, the eutectic point is nearer the respective silver halide, i.e., the component having a higher melting point. This feature is a very rare occurrence in the binary phase diagrams of the simple eutectic type.[15,16]

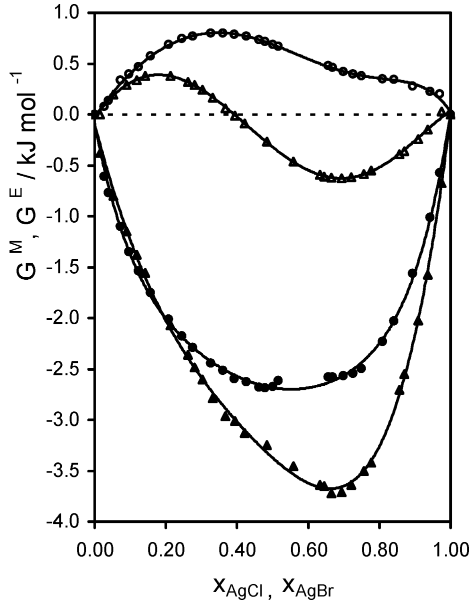

Figure 4. Molar free enthalpy of mixing G^M for molten solutions: ▲, $ZnCl_2$ + AgCl; ●, $ZnBr_2$ + AgBr. Molar excess free enthalpy G^E for molten solutions: △, $ZnCl_2$ + AgCl; ○, $ZnBr_2$ + AgBr.

It can be seen that in the systems under study the deviations from the ideal solution behavior are generally not considerable. Their absolute values for both systems are similar. However, they show different signs and changes with composition in the chloride and in the bromide solutions.

It has been found that for the $ZnBr_2$ + AgBr system, deviations from Raoult's law are positive over the whole concentration range. The integral molar excess free enthalpy shows a maximum of 800 J mol^{-1} at about 0.4 mol fraction of AgBr. In the $ZnCl_2$ + AgCl system, deviations from Raoult's law are positive only in solutions rich in zinc chloride. The integral molar excess free enthalpy shows a maximum of 380 J mol^{-1} at about 0.2 mol fraction of AgCl and crosses zero at about 0.4 mol fraction of AgCl. A minimum of −625 J mol^{-1} is at about 0.7 mol fraction of AgCl. The negative deviations from the ideal solution behavior in the $ZnCl_2$ + AgCl system, in contrast to the positive ones in the $ZnBr_2$ + AgBr system, may be attributed to formation of stronger complexes in molten mixtures of zinc chloride and silver chloride, especially in mixtures with higher content of silver chloride.

The integral molar enthalpies of mixing at 768 K and 928 K for the liquid AgCl + $ZnCl_2$ system were determined by Papatheodorou and Kleppa[17] using a high-temperature twin microcalorimeter. The enthalpies of mixing obtained are positive and asymmetric, with the more endothermic values at high zinc chloride concentrations, and they are less positive at the higher temperature. This behavior is consistent with a network-type structure of molten zinc chloride revealed by a number of different experimental techniques such as neutron and X-ray diffraction[18−21] and Raman spectroscopy[1,22,23] as well as by modeling and simulation studies.[24−26]

We used the known enthalpies of mixing in liquid mixtures of zinc chloride with silver chloride[17] to estimate the entropies of mixing in these mixtures along the liquidus curves. A linear change of the enthalpies of mixing with temperature was assumed. The integral molar entropies of mixing S^M, the integral molar excess entropies of mixing S^E, and the integral molar entropies of mixing for the ideal solution $S^{M,id}$ are plotted against mole fraction in Figure 5. Higher entropy of mixing is found in solutions with

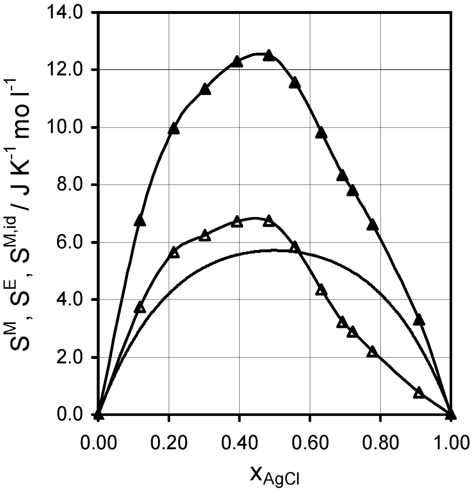

Figure 5. Molar entropy of mixing S^M (▲) and excess molar entropy of mixing S^E (△) for molten solutions $ZnCl_2 + AgCl$; molar entropy of mixing for the ideal solution $S^{M,id}$ (solid line).

higher concentration of zinc chloride, which may be connected with structural changes as the pure liquid zinc chloride is diluted with silver chloride. Lower entropy of mixing in solutions with higher concentration of silver chloride may indicate the possibility of complex formation in these mixtures.

Conclusions

It was shown that equilibrium phase diagrams for the $ZnCl_2 + AgCl$ and $ZnBr_2 + AgBr$ systems are of the simple eutectic type and that solid solubility is negligible. This allowed for the calculation of thermodynamic activities and free enthalpies of mixing in liquid solutions in the entire range of compositions for both systems.

The integral molar excess free enthalpy for the $ZnBr_2 +$ AgBr system was found to be positive over the whole concentration range. The integral molar excess free enthalpies for the $ZnCl_2 + AgCl$ system are negative for solutions rich in AgCl, indicating a stronger tendency to formation of complexes in the chloride cases. However, deviations from the ideal solution behavior are generally not considerable in the systems under study.

Results of estimation of the entropies of mixing in the molten $ZnCl_2 + AgCl$ system are in accordance with the network structure of the pure liquid zinc chloride and possible formation of complexes in mixtures with higher concentration of silver chloride.

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