Densities and Molar Excess Volumes of Molten (Alk, Ag)Br- and (Alk, Ag)I-Mixtures

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Measurements of densities (and from these molar excess volumes) of the molten salt systems (K,Ag)Br, (Na,Ag)Br, (Rb,Ag)Br, (Cs,Ag)Br, (Na,Ag)I, (K,Ag)I, and (Cs,Ag)I as functions of composition and temperature from the liquidus curve up to 1200 K are reported.

Our method of measuring the densities of molten salts is described in [1]. The results have been fitted to the equation

$$\varrho(T, x_2) = (a + b x_2 + c x_2^2 + d x_2^3) + (a' + b' x_2 + c' x_2^2 + d' x_2^3)\, T\,, \quad (1)$$

where ϱ denotes the density, T the absolute temperature, and x_2 the mole fraction of the silver component.

The obtained coefficients $a, b, c, d, a', b', c', d'$ are listed in Table 1. The molar excess volumes were evaluated from the equations

$$\bar{V}_{\text{add.}} = (1 - x_2)\frac{M_1}{\varrho_1} + x_2\frac{M_2}{\varrho_2}\,, \quad (2)$$

$$\bar{V} = [(1 - x_2)\, M_1 + x_2 M_2]/\varrho \quad (3)$$

and

$$\overline{V^{\text{E}}} = \bar{V} - \bar{V}_{\text{add.}}\,, \quad (4)$$

where M_1 and M_2 are the molar weights and ϱ_1 and ϱ_2 the densities of the pure salts.

The excess volumes of the (Alk, Ag)Br- and (Alk, Ag)I-mixtures are listed in Tables 2, and plotted in Figure 1. Depending on their composition, the (Alk, Ag)Br systems have positive and negative excess volumes. In contrast to the (Alk, Ag)Br- and (Alk, Ag)Cl-systems [1], all investigated (Alk, Ag)I systems have negative excess volumes.

The volume fraction of component 2 is defined as

$$\Psi_2 = x_2\frac{M_2}{\varrho_2}\left[(1 - x_2)\frac{M_1}{\varrho_1} + x_2\frac{M_2}{\varrho_2}\right]. \quad (5)$$

Some deviations from linearity are shown in Figures 2 and 3. With the exception of (Na, Ag)I, for the (Alk, Ag)Cl- [1], (Alk, Ag)Br-, (Alk, Ag)I-

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Table 1. Constants for the calculation of the densities of the molten (Alk, Ag)I- and (Alk, Ag)Br-mixtures, depending on composition and temperature.

	(Na, Ag)I	(K, Ag)I	(Cs, Ag)I	
a (g cm^{-3})	3.56847	3.17252	3.92596	
b (g cm^{-3})	2.38356	3.58116	3.58490	
c (g cm^{-3})	1.52402	−1.99325	−2.86987	
d (g cm^{-3})	−1.11780	1.66507	1.77602	
a' ($\cdot 10^3$ g cm^{-3})	−0.89785	−0.79940	−0.91824	
b' ($\cdot 10^3$ g cm^{-3})	−0.18664	−1.15796	−1.90151	
c' ($\cdot 10^3$ g cm^{-3})	−0.76515	1.72076	2.26142	
d' ($\cdot 10^3$ g cm^{-3})	0.86072	−0.78801	−0.44250	
	(Na, Ag)Br	(K, Ag)Br	(Rb, Ag)Br	(Cs, Ag)Br
a (g cm^{-3})	3.20989	2.96403	3.74662	4.27735
b (g cm^{-3})	2.47619	3.72788	1.58203	−0.39662
c (g cm^{-3})	1.39961	−1.67602	0.84282	3.70048
d (g cm^{-3})	−0.76801	1.26602	0.14070	−1.22769
a' ($\cdot 10^3$ g cm^{-3})	−0.83611	−0.82130	−1.05919	−1.22946
b' ($\cdot 10^3$ g cm^{-3})	−0.39076	−1.76399	−0.35752	1.27793
c' ($\cdot 10^3$ g cm^{-3})	−0.76457	2.11354	0.18654	−3.82505
d' ($\cdot 10^3$ g cm^{-3})	0.56445	−0.50536	0.18759	2.72832

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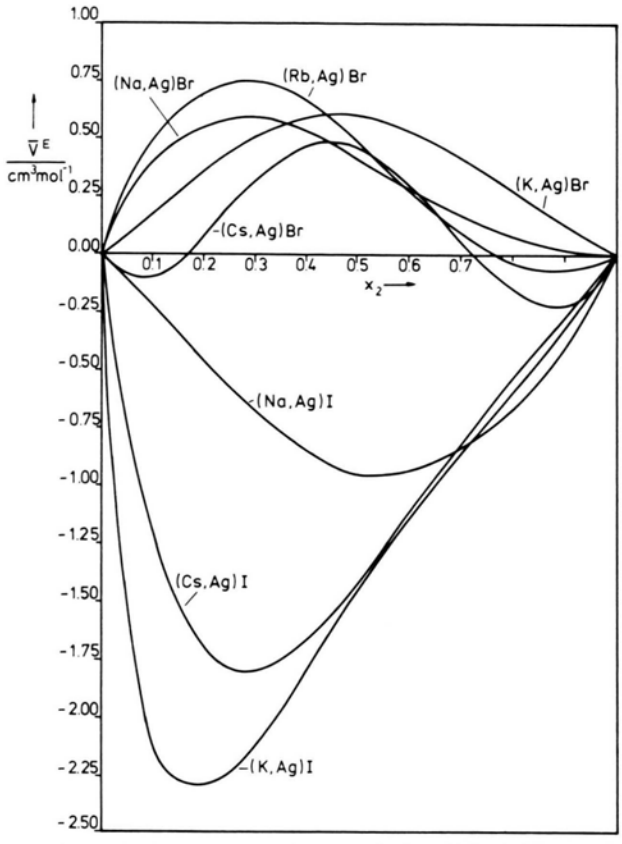

Fig. 1. Molar excess volumes of the (Alk, Ag)Br- and (Alk, Ag)I-mixtures at 1050 K.

Table 2. Molar excess volumes $\overline{V^E}$ of (Alk, Ag)Br- and (Alk, Ag)I-mixtures at 1050 K in units cm^3/mol.

	(K, Ag)Br	(Na, Ag)Br	(Rb, Ag)Br	(Cs, Ag)Br
0	0	0	0	0
0.1	0.302	0.413	0.525	−0.264
0.2	0.561	0.594	0.766	−0.118
0.3	0.731	0.620	0.806	0.150
0.4	0.800	0.553	0.702	0.354
0.5	0.770	0.438	0.513	0.397
0.6	0.663	0.308	0.296	0.275
0.7	0.501	0.187	0.099	0.052
0.8	0.317	0.088	−0.035	−0.160
0.9	0.141	0.024	−0.076	−0.222
1	0	0	0	0

	(Na, Ag)I	(K, Ag)I	(Cs, Ag)I
0	0	0	0
0.1	−0.249	−1.165	−0.744
0.2	−0.498	−1.669	−0.955
0.3	−0.716	−1.777	−0.883
0.4	−0.871	−1.658	−0.696
0.5	−0.949	−1.423	−0.506
0.6	−0.941	−1.130	−0.362
0.7	−0.842	−0.847	−0.275
0.8	−0.652	−0.560	−0.229
0.9	−0.371	−0.282	−0.151
1	0	0	0

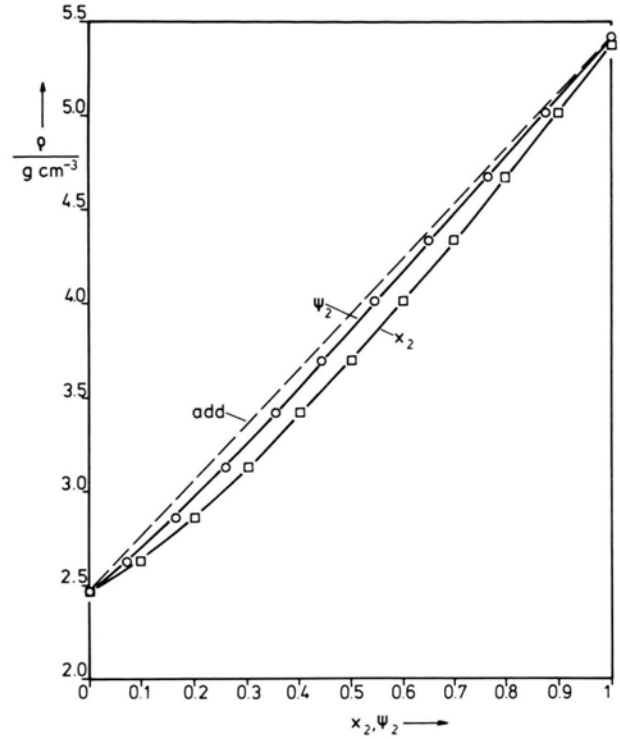

Fig. 2. The densities ϱ of (Na, Ag)Br plotted against x_2 and Ψ_2 at 1050 K.

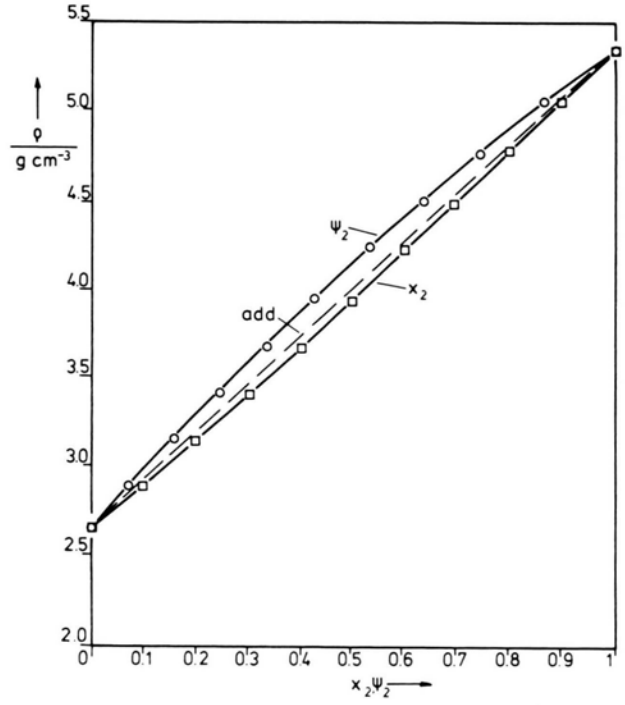

Fig. 3. The densities ϱ of (Na, Ag)I plotted against x_2 Ψ_2 at 1050 K.

systems the dependence of ϱ on Ψ_2 is more nearly linear than that of ϱ on x_2.

With our experimental setup we also tried to investigate the system (Rb, Ag)I. The molten salt mixtures of this system heavily evolve vapour, which influences the measurements so that they are not reported here.

[1] A. Krekelberg, W. Merkens, and J. Richter, Z. Naturforsch. **38a**, 890 (1983).

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