The interdiffusion in liquid alloys of alkali metals with lead

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Abstract. The mutual diffusion in liquid cesium-lead alloys containing from 20 to 70 at.% Pb is investigated by a gamma-ray attenuation technique. The obtained data are compared with the results of similar studies for Li-Pb, Na-Pb, and K-Pb melts, carried out by us earlier. The concentration dependences of the interdiffusion coefficient for alkali-lead liquid systems demonstrate pronounced maxima in the vicinity of 20 or 50 at.% Pb. These phenomena confirm a tendency for chemical short-range ordering in liquid alloys.

1. Introduction
Liquid alloys of lead with alkali metals belong to systems in which, apart from the metallic type of chemical bond, partial ionic bonding is observed, which is due to the large difference in electronegativity between the lead and alkali elements [1]. The compositional dependencies of thermophysical and electrical properties of these liquid systems demonstrate pronounced extrema near 20 or 50 at.% Pb [1-5]. According to modern concepts, these effects are associated with a tendency for forming ionic complexes in the melts [1]. It is assumed that the Li–Pb and Na–Pb systems mainly contain the Li⁺₄Pb⁻⁴ and Na⁺₄Pb⁻⁴ complexes. In the alloys of the lead with potassium, rubidium, and cesium, polyanionic complexes are believed to prevail. This compound consists of Pb₄⁺ tetrahedron and four cations of alkali elements. The concentration of the complexes of the first and second types reaches a maximum in the melts with compositions close to stoichiometric (20 and 50 at. % Pb, respectively), which leads to anomalies in the concentration dependences of structure-sensitive properties at these percentages. The theory of this phenomenon (sometimes called the "concentration-driven metal-nonmetal transition") has not been fully developed at the moment. This is primarily due to the lack of experimental data on many structure-sensitive properties of liquid alloys, which reveal mixed (metallic and ionic) interatomic bonding. In particular, the viscosity, thermal conductivity, and interdiffusion in many alkali-lead liquid systems have not been investigated so far.

This work aims to measure the coefficients of interdiffusion in Cs-Pb melts within wide ranges of concentrations and temperatures, and to compare the obtained data with the results of similar studies for liquid Li-Pb, Na-Pb, and K-Pb systems, which we performed earlier [3-5].

2. Experimental technique
Mutual diffusion in the cesium-lead melts was investigated by a gamma-ray attenuation method. In this method, the kinetics of homogenization of liquid alloy was determined from experimental data on the radiation attenuation in the sample at various heights. The details of the experimental equipment and procedures have been described elsewhere [3-5]. The diffusion tests were performed with the samples, which were used earlier for the density measurement of the Cs-Pb alloys [2]. The cesium and
lead used for the preparation of the samples were 99.9 and 99.99 wt.% purity, respectively. Hermetic cells for the alloys were made of stainless steel. The free volume of the cells was filled with argon. The sample was melted and heated to the temperature at which the diffusion experiment was conducted. The concentration and density differences in the inhomogeneous liquid alloy gradually decreased due to diffusion. The rate of relaxation of the concentration and density was measured near the upper and lower borders of the melt column. The data on the relaxation served to obtain the coefficient of interdiffusion $D$.

3. Results and discussion
The obtained data for the mutual diffusion coefficients in cesium-lead liquid alloys are shown in table 1. For the samples containing 50 and 55 at.% Pb, the diffusion test was carried out only at a single temperature. The composition of the other samples was markedly different from the compositions of intermediate compounds and eutectics in the cesium-lead system. After crystallization and subsequent melting, such an alloy became inhomogeneous again due to the effect of liquation. This allowed performing several diffusion experiments with a single sample at different temperatures.

Table 1. The experimental coefficients of interdiffusion in the Cs-Pb liquid alloys.

| Composition, at. % Pb | Temperature, K | $D$, $10^{-5}$ cm$^2$/s |
|----------------------|----------------|------------------------|
| 20.0                 | 774.4          | 3.9 ± 0.1              |
| 20.0                 | 900.5          | 6.8 ± 0.2              |
| 20.0                 | 1021.1         | 9.8 ± 0.4              |
| 30.1                 | 830.5          | 4.6 ± 0.2              |
| 30.1                 | 940.5          | 7.9 ± 0.1              |
| 30.1                 | 1025.1         | 10.6 ± 0.5             |
| 40.0                 | 822.7          | 8.5 ± 1.3              |
| 40.0                 | 911.3          | 14.7 ± 3.1             |
| 40.0                 | 988.3          | 18.5 ± 5.9             |
| 40.0                 | 1022.0         | 22.7 ± 7.0             |
| 45.0                 | 940.6          | 28.1 ± 10.0            |
| 45.0                 | 988.3          | 18.5 ± 6.0             |
| 45.0                 | 1015.5         | 18.0 ± 0.4             |
| 50.0                 | 935.7          | 30.2 ± 2.7             |
| 55.0                 | 940.6          | 18.1 ± 5.0             |
| 70.0                 | 869.5          | 2.4 ± 0.2              |
| 70.0                 | 1006.7         | 5.4 ± 0.4              |

The main error in the $D$ values comes from the random uncertainty in the measured gamma radiation intensity and the systematic uncertainty in the height of the melt column. In some cases, a significant contribution to $\Delta D$ is made by a methodological error. The origin of this error is discussed in detail in [3].

The experimental values of $D$ for the compositions of 20.0 and 30.1 at.% Pb as a function of temperature $T$ are shown in figure 1. Within the measurement error, the $D(T)$ dependences are linear within the temperature range under study.
Figure 1. Temperature dependences of the interdiffusion coefficient for liquid Cs$_{80}$Pb$_{20}$ and Cs$_{70}$Pb$_{30}$ alloys. The points are the experimental data. The lines are the best linear fits to the data points.

Figure 2 shows the estimated compositional dependency of the interdiffusion coefficient for the liquid cesium-lead system, constructed from the experimental data. For comparison, analogous dependencies for Li-Pb, Na-Pb, and K-Pb melts, which we studied earlier [3-5], are also shown in the plot. As is seen, all curves have maxima near 20 at.\% Pb (Li-Pb, and Na-Pb) or near 50 at.\% Pb (K-Pb, and Cs-Pb), which is evidence of a marked change in the structure of the liquid alloys in these concentration regions.

To reveal the features in the structure of liquid alloys, the Darken stability function, $S = \partial^2 \Delta G / \partial X^2$, is widely used ($\Delta G$ is Gibbs free energy of mixing, and $X$ is an atomic composition of the alloy) [6]. The presence of maxima in the $S(X)$ dependence shows a tendency to heterocoordination (or, in other words, a tendency to forming associated complexes in the melts). The experimental $S(X)$ dependences for the alkali-lead liquid systems indicate the presence of two types of complexes (with stoichiometric ratios of 4:1 and 1:1) [7]. The interdiffusion coefficient is related with the stability by Darken’s equation [6]:

$$(D/D_{id}) = (RT)^{-1}X(1 - X)S,$$

where $D_{id}$ is the interdiffusion coefficient of the hypothetic ideal solution with the same components, and $R$ is gas constant. Then, the presence of extrema in the $S(X)$ dependence should lead to the same features in the $D(X)$ curve. The maxima in the concentration dependences of the interdiffusion coefficient and stability function for the alkali-lead melts are indeed observed at the same compositions. Thus, the mutual diffusion data confirm a tendency for forming “liquid compounds” with a stoichiometric ratio of 4:1 in the Li-Pb and Na-Pb alloys, and with a stoichiometric ratio of 1:1 in the K-Pb and Cs-Pb alloys.
Figure 2. Mutual diffusion coefficients of liquid alkali-lead systems as a function of composition (data from [3-5] and the present study).

4. Conclusion
The first experimental data on the coefficients of interdiffusion have been obtained for liquid cesium-lead alloys in a wide range of concentrations and temperatures. Analysis of the data confirms a tendency for compound formation in the liquid alkali-lead systems.

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