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REDUCTION OF EINSTEINIUM AND CALIFORNIUM CHLORIDES TO THE DIVALENT STATE IN AQUEOUS ETHANOLIC SOLUTIONS

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According to some views found in literature einsteinium and californium can be prepared in divalent state (1 - 6). With this task in mind, it was necessary to find a system in which a high reduction potential could be created, the divalent form of the actinide stabilized and, finally, the reliable identification of the Me^{2+} state of the actinide present in microamounts done. All these requirements are met by the process of simultaneous reduction of samarium chlorides and the actinide under study by magnesium metal in aqueous ethanolic solutions when low soluble $SmCl_2$ formed takes up the divalent actinide. The true isomorphous cocrystallization which takes place in this case makes it possible both to identify and stabilize the actinide in the divalent state, since the Me^{2+} actinide forms a part of the matrix of the $SmCl_2$ crystal lattice.

In order to identify the divalent state of actinide elements it was necessary to carry out a quantitative analysis of their cocrystallization with $SmCl_2$. We have conducted the experiments in the following way. I ml of an ethanolic solution of samarium chloride containing approximately 50 mg/ml of Sm^{3+} and some quantities of the element under study and strontium-85 without a carrier were placed in a special graduated test tube. Then 50 mg of magnesium turning and I ml of a 7M solution of hydrogen chloride in ethanol were added. As a result of the reaction a red crystalline $SmCl_2$ precipitate was formed carrying Es, Cf and Sr. The degree of Sm precipitation changed from experiment to experiment and ranged from 10 to 20 per cent.

We have examined the distribution of one microelement, e.g. Es or Cf, in relation to the other microelement - strontium - between the $SmCl_2$ precipitate and the solution. The relative distribution took place in accordance with equation 1, obtained on the basis of semi-logarithmic equations of cocrystallization (7,8) of each microelement with $SmCl_2$.

$$\ln \frac{a}{a - x} = \lambda \cdot \ln \frac{b}{b - y} \qquad (1)$$ where

a and b - the quantities of one and the other microelement in the system;

x and y - their content in the $SmCl_2$ precipitate; and

λ - the distribution coefficient. The λ value is a constant with constant thermodynamical parameters of the system and also on condition that the charges of the ions of the two microelements are identical. If, on the contrary, together with the cocrystallizing form of the Me^{2+} microelement its non-cocrystallizing form,e.g. Me^{3+}, is present, a lower $[Me^{2+}] / [Me^{3+}]$ value will result in a lower λ value. Since $[Me^{2+}] / [Me^{3+}] = f([Sm^{2+}] / [Sm^{3+}])$, with the constant Sm^{3+} concentration, the λ value will grow with an increasing $[Sm^{2+}]$ value.

The reduction of Es and Cf in a solution to the divalent state will be proved if we determine that both of these microelenemts cocrystallize with $SmCl_2$ due to true isomorphism. To do this, the influence of an admixture of $LaCl_3$ which is the salt of an easily sorbated cation, on the distribution coefficient has been examined. Besides, the Me/Sr distribution coefficients have been compared for the case of crystallization and recrystallization of a separately prepared $SmCl_2$ precipitate. The difference between these experiments is that with the crystallization a higher Sm^{2+} concentration is achieved than with the recrystallization of the separately prepared precipitate owing to the formation of a super-saturated $SmCl_2$ solution during the crystallization. Finally, a study has been made of the yttrium cocrystallization with $SmCl_2$, an element which is not known to exist in the divalent state, and Eu which qualitatively is converted to the divalent state when Sm^{3+} is reduced to Sm^{2+}. The results obtained are given in Table 1.

TABLE I

Distribution coefficients of the investigated microelements in relation to Sr microquantities with crystallization and recrystallization of $SmCl_2$ x/

Element	Crystallization of precipitate	Recrystallization of precipitate
Y^{88}	0.004 ± 0.001	-
Eu^{155}	1.3 ± 0.2 1.5 ± 0.3 xx/	1.8 ± 0.5
Es^{253}	0.15 ± 0.01 0.26 ± 0.04 xx/	0.020 ± 0.003
Cf^{252}	0.026 ± 0.003 0.048 ± 0.012 xx/	0.007 ± 0.002

x/ 68% confidence limits

xx/ Crystallized with $LaCl_3$ present,
[La] - I mg/ml.

The results of the experiments show that

1. Yttrium-88 practically does not cocrystallize with $SmCl_2$ and an admixture of $LaCl_3$ does not reduce the Eu, Es and Cf distribution coefficients.
2. The Eu distribution coefficient with crystallized and recrystallized $SmCl_2$ is constant, whereas the Es and Cf distribution coefficients are higher with crystallized $SmCl_2$ than with the recrystallized separately prepared precipitate.

From point I it follows that the cocrystallization of Es and Cf with $SmCl_2$ is due to true isomorphism. Therefore, these elements are reduced together with samarium to the divalent state.

From point 2 it follows that Es and Cf are reduced only partially when $SmCl_2$ is formed. Hence, the proximity of the standard oxidation-reduction potentials of $Me^{2+} \rightleftharpoons Me^{3+} + e$ of these elements to that of samarium.

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