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Correlation between Oxidation Potentials of the Lanthanides in Aqueous Solutions and Chloride Melts

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Abstract

Based on the literature and experimental data obtained by the authors, it appears that the differences in the oxidation potentials of the M^{3+}/M^{2+} couples for two f-elements in chloride melts and in some other solvents coincide with the differences in the standard oxidation potentials of the M^{3+}/M^{2+} couples for the same elements in aqueous solutions. Also, a dependence between the solubility of the metals of f-elements, in their molten trichlorides and the standard oxidation potential values of the M^{3+}/M^{2+} and M^{3+}/M^0 couples for aqueous solutions has been established. The correlation determined enabled us to plot a single scale of the standard oxidation potentials of the M^{3+}/M^{2+} couples for f-elements as well as calculate the metal solubilities in their molten trichlorides.

Introduction

In our previous studies [1–11] we have determined the differences in the formal oxidation potentials of the M^{3+}/M^{2+} couples for various f-elements in ethanolic media at a temperature of 298 K and in chloride melts at a temperature of 1173 K (see Table I). Also, there are literature data (see refs. 12–18) for the formal and standard oxidation potential values of the M^{3+}/M^{2+} couples for the lanthanides and actinides which reduce rather easily in chloride melts as well as in other solvents. Based on these data, we found the differences in the oxidation potentials of the M^{3+}/M^{2+} couples ($\Delta E_{M_1-M_2} = E_{M_1{}^{3+}/M_1{}^{2+}} - E_{M_2{}^{3+}/M_2{}^{2+}}$).

TABLE I. Oxidation Potential Differencies $\Delta E_{M-m} = E_{M^{3+}/M^{2+}} - E_{m^{3+}/m^{2+}}$ in Molten Salts.[a]

Element Couple	$E_{M-m} = E_{M^{3+}/M^{2+}} - E_{m^{3+}/m^{2+}}$ (V)	
Pr–Ce	+0.08 ± 0.04	[1]
Pr–Nd	−0.22 ± 0.04	[2]
Pr–Gd	+0.01 ± 0.03	[3]
Pr–Tb	−0.01 ± 0.03	[3]
Pr–Cm	−0.06 ± 0.02	[4]
Pr–La	$+0.10 \pm^{0.03}_{0.05}$	[5]
Pr–Lu	$-0.12 \pm^{0.02}_{0.04}$	[5]
Nd–Pm	−0.18 ± 0.02	[6]
Nd–Dy	−0.07 ± 0.04	[7]
Nd–Pu	−0.03 ± 0.03	[8]
Nd–Am	−0.34 ± 0.03	[6]
Nd–Bk	−0.10 ± 0.01	[6]
Sm–Yb	−0.31 ± 0.02	[7]
Sm–Cf	+0.13 ± 0.02	[7]
Sm–Es	−0.05 ± 0.01	[7]
Sm–Fm	−0.32 ± 0.01	[7]
Ho–Dy	−0.26 ± 0.03	[9]
Ho–Er	+0.08 ± 0.06	[9]
Ho–Tm	−0.38 ± 0.15	[9]

[a] M is macrocomponent; m is microcomponent.

The oxidation potential differences ($\Delta E_{M_1-M_2}$) of the M^{3+}/M^{2+} couples obtained by us experimentally and calculated based on the literature data enabled us to compare these values for certain element couples (see Table II). As is shown in Table II, $\Delta E_{M_1-M_2}$ for respective elements remain constant within the experiment error and do not depend either on the nature of the liquid phase, or on the temperature. The phenomenon discovered is of real interest and requires consideration.

The oxidation potential of an M^{3+}/M^{2+} couple is known to be related to a number of thermodynamical parameters according to the following equation:

$$F(E_{M^{3+}/M^{2+}} + E_e)$$

$$= \Delta G_{ion}(M^{2+}) + \Delta G_{solv}(M^{3+}) - \Delta G_{solv}(M^{2+})$$

where $E_{M^{3+}/M^{2+}}$ is the oxidation potential of the

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TABLE II. Differencies in the Oxidation Potentials of the M^{3+}/M^{2+} Couples in Solutions and Melts.

Element Couple	Oxidation Potential Differences (V)					
	Water	Ethanol		Acetonitrile	Chloride Melts	
	Electrochem.	Thermochem.	Cocrystalliz.	Electrochem.	Cocrystalliz.	Electrochem.
Sm–Yb	−0.40 ± 0.02 [13] −0.32 ± 0.01 [15]	−0.36 ± 0.08 [14]			−0.31 ± 0.02 [7]	−0.354 ± 0.007 [12]
Sm–Eu	−1.20 ± 0.03 [13] −1.16 ± 0.01 [15]	−1.06 ± 0.08 [14]		−1.2 [16]		−1.175 ± 0.009 [12]
Yb–Eu	−0.80 ± 0.03 [13] −0.84 ± 0.01 [15]	−0.70 ± 0.08 [14]				−0.821 ± 0.008 [12]
Nd–Dy		−0.06 ± 0.08 [14]			−0.07 ± 0.04 [7]	
Yb–Fm			0 ± 0.02 [10]		0.01 ± 0.02 [7]	
Sm–Es			0 ± 0.04 [11]		−0.05 ± 0.01 [7]	
Sm–Cf	−0.09 ± 0.05 [17]		0.05 ± 0.04 [11]	0.03 [18]	0.13 ± 0.02 [7]	

M^{3+}/M^{2+} couple, E_e is the thermodynamical electrode potential of the reference electrode, F is the Faraday constant, $\Delta G_{ion}(M^{2+})$ is the change in free energy of ionization of double-charged ions in the gaseous phase (calculated from the third ionization potential value I_3 [19]), $\Delta G_{solv}(M^{3+})$ and $\Delta G_{solv}(M^{2+})$ are the free energy changes at the interaction of triple- and double-charged ions with the liquid phase [20].

It follows that the difference in the oxidation potentials of the M^{3+}/M^{2+} couples for any two elements, M_1 and M_2, can be expressed by the following eqn.:

$$
\begin{aligned}
F\Delta E_{M_1-M_2} = {} & \Delta G_{ion}(M_1{}^{2+}) - \Delta G_{ion}(M_2{}^{2+}) \\
& + \Delta G_{solv}(M_1{}^{3+}) - \Delta G_{solv}(M_2{}^{3+}) \\
& - \Delta G_{solv}(M_1{}^{2+}) - \Delta G_{solv}(M_2{}^{2+}) \qquad (2)
\end{aligned}
$$

When considering a couple of elements in two oxidation states and in different liquid phases and at different temperatures, the difference of $\Delta E_{M_1-M_2} - \Delta E'_{M_1-M_2}$ (the stress $'$ refers to the other phase and temperature) would be in accordance with the following eqn.:

$$
\begin{aligned}
F(\Delta E_{M_1-M_2} - \Delta E'_{M_1-M_2}) = {} & [\Delta G_{ion}(M_1{}^{2+}) \\
& - \Delta G'_{ion}(M_1{}^{2+})] - [\Delta G_{ion}(M_2{}^{2+}) - \Delta G'_{ion}(M_2{}^{2+})] \\
& + [\Delta G_{solv}(M_1{}^{3+}) - \Delta G'_{solv}(M_1{}^{3+})] \\
& - [\Delta G_{solv}(M_2{}^{3+}) - \Delta G'_{solv}(M_2{}^{3+})] \\
& - [\Delta G_{solv}(M_1{}^{2+}) - \Delta G'_{solv}(M_1{}^{2+})] \\
& + [\Delta G_{solv}(M_2{}^{2+}) - \Delta G'_{solv}(M_2{}^{2+})] \qquad (3)
\end{aligned}
$$

$$
\begin{aligned}
F\delta E_{M_1-M_2} = {} & [\delta G_{ion}(M_1{}^{2+}) - \Delta G_{ion}(M_2{}^{2+})] \\
& + \{\delta G_{solv}(M_1{}^{3+}) - \delta G_{solv}(M_2{}^{3+}) \\
& - \delta G_{solv}(M_1{}^{2+}) + \delta G_{solv}(M_2{}^{2+})\} \qquad (4)
\end{aligned}
$$

Based on the analysis of this eqn. it is evident that at the same temperature but in different liquid phases $\delta G_{ion}(M_1{}^{2+}) = \delta G_{ion}(M_2{}^{2+}) = 0$ by definition. Then, $\delta E_{M_1-M_2} = 0$ if the sum of the values in figure brackets of eqn. (4) equals zero. The constancy of $\Delta E_{M_1-M_2}$ for Sm–Eu and Sm–Cf couples in water, ethanol and acetonitrile may serve as an example (see Table II). In the case of the same liquid phase but different temperatures $\delta G_{solv}(M_1{}^{3+}) \approx \delta G_{solv}(M_2{}^{3+})$, and $\delta G_{solv}(M_1{}^{2+}) \approx \delta G_{solv}(M_2{}^{2+})$ by definition and, therefore, $\delta E_{M_1-M_2} = 0$ provided the same temperature changes in the third ionization potential I_3 of the compared elements. The Sm–Yb couple in chloride melts serves as an example. The value of $\Delta E_{M_1-M_2}$ in the experiments conducted at the temperature of 1173 K [7] and 723 K [12] was constant.

The discovered correlation dependences are apparently accounted for by the chemical closeness of the f-elements. Similar properties are characteristic of many analogous elements so that the f-elements are not an exception in this way. Previous work [21] provides data on normal electrode potentials for some elements in aqueous and non-aqueous solutions. Therefore we can derive the values $\Delta E_{M_1-M_2} = E_{M_1{}^{n+}/M_1{}^{0}} - E_{M_2{}^{n+}/M_2{}^{0}}$ (see Table III) for the elements which are close by their chemical properties. Table III indicates that the differences in the normal electrode potentials in different solvents for these elements remain almost constant. So it follows that when provided with the values of the standard potentials of the $M_1{}^{3+}/M_1{}^{2+}$ couples for certain lanthanides as well as the values of $\Delta E_{M_1-M_2}$, measured by us,

TABLE III. Differences in the Normal Electrode Potentials in Various Solvents ($E^0_{M_1^{n+}/M_1^0} - E^0_{M_2^{n+}/M_2^0}$) Relative to the Normal Hydrogen Electrode in Water [21].

Electrode Couple	$E^0_{M_1^{n+}/M_1^0} - E^0_{M_2^{n+}/M_2^0}$ (V)			
	Ammonium hydroxide	Water	Methanol	Ethanol
$Li^+/Li-Na^+/Na$	0.39	0.24	0.32	0.36
$Na^+/Na-K^+/K$	−0.13	−0.21	−0.14	−0.17
$Zn^{2+}/Zn-Cd^{2+}/Cd$	0.33	0.30	0.31	0.26

TABLE IV. Standard Oxiation Potential Values of the M^{3+}/M^{2+} Couples for the Lanthanides and Actinides.

Ln	$E^0_{Ln^{3+}/Ln^{2+}}$ (V)	An	$E^0_{An^{3+}/An^{2+}}$ (V)
La	−2.94 ± 0.08	Ac	Not available
Ce	−2.92 ± 0.08	Th	Not available
Pr	−2.84 ± 0.06	Pa	Not available
Nd	−2.62 ± 0.06 [14]	U	Not available
Pm	−2.44 ± 0.05	Np	Not available
Sm	−1.50 ± 0.01 [15]	Pu	−2.59 ± 0.06
Eu	−0.34 ± 0.01 [15]	Am	−2.28 ± 0.06
Gd	−2.85 ± 0.07	Cm	−2.78 ± 0.07
Tb	−2.83 ± 0.07	Bk	−2.52 ± 0.05
Dy	−2.56 ± 0.05 [14]	Cf	−1.63 ± 0.02
Ho	−2.79 ± 0.06	Es	−1.45 ± 0.01
Er	−2.87 ± 0.08	Fm	−1.18 ± 0.02
Tm	−2.22 ± 0.05 [14]	Md	−0.15 ± 0.05 [13]
Yb	−1.18 ± 0.01 [15]	No	+1.45 ± 0.05 [13]
Lu	−2.72 ± 0.07		

in chloride melts and some other solvents, we can determine the previously unknown values of the standard oxidation potentials of the M_2^{3+}/M_2^{2+} couples for the f-elements and make up a potential scale (see Table IV).

Recently, M–MCl_3 phase diagrams for many f-elements have been studied. They indicate that the metallic lanthanides and actinides dissolve in their respective trihalogenide melts to a greater or lesser extent. This phenomenon may be viewed as a oxidation-reduction process: $M + 2MCl_3 \rightleftharpoons 3MCl_2$. Since in these systems an element is present in its three oxidation states (M^0, M^{2+}, M^{3+}) in the state of equilibrium, we can propose the following eqn.:

$$E_{M^{3+}/M^{2+}}\,(T = 1173\text{ K}) + \left(\frac{RT}{F}\ln\frac{[M^{3+}]}{[M^{2+}]}\right) = E_{M^{3+}/M^0}\,(T = 1173\text{ K}) + \left(\frac{RT}{3F}\ln\,[M^{3+}]\right) \qquad (5)$$

In this eqn. the values of $E_{M^{3+}/M^{2+}}$ and E_{M^{3+}/M^0} in molten salts at the temperature of 1173 K are unknown. As shown above, however, $\Delta E_{M_1-M_2}$, in the case of the lanthanides and actinides, does not depend on either the temperature or on the composition of the liquid phase. Therefore the oxidation potential of an M^{3+}/M^{2+} couple in the melt at the temperature of 1173 K and the standard oxidation potential of the same couple in an aqueous solution at the temperature of 298 K would differ from each other by some constant value:

$$E_{M^{3+}/M^{2+}}\,(T = 1173\text{ K}) - E^0_{M^{3+}/M^{2+}}\,(T = 298\text{ K}) = a$$

Considering this we could write down an eqn. for the oxidation potentials of the M^{3+}/M^0 couple:

$$E_{M^{3+}/M^0}\,(T = 1173\text{ K}) - E^0_{M^{3+}/M^0}\,(T = 298\text{ K}) = b$$

Substituting $E_{M^{3+}/M^{2+}}$ (T = 1173 K) and E_{M^{3+}/M^0} (T = 1173 K) in eqn. (5) for the respective values of the standard oxidation potentials we arrive at the following eqn.:

$$E^0_{M^{3+}/M^{2+}}\,(T = 298\text{ K}) + \left(\frac{RT}{F}\ln\frac{[M^{3+}]}{[M^{2+}]}\right) + a = E^0_{M^{3+}/M^0}\,(T = 298\text{ K}) + \left(\frac{RT}{3F}\ln\,[M^{3+}]\right) + b \qquad (6)$$

and we can thus calculate the value of $a - b$:

$$a - b = E^0_{M^{3+}/M^0} - E^0_{M^{3+}/M^{2+}} + \left(\frac{RT}{3F}\ln[M^{3+}]\right) - \left(\frac{RT}{F}\ln\frac{[M^{3+}]}{[M^{2+}]}\right) \qquad (7)$$

Table V gives mole fractions $[M^{3+}]$ and $[M^{2+}]$ calculated based on the solubility of a metal in the melt of its trichloride at the temperature of 1173 K [22] and on the standard oxidation potentials of the M^{3+}/M^{2+} couples (see Table IV) and of the M^{3+}/M^0 couples [23]. Also, the table presents the $a - b$ values for some lanthanides and actinides calculated based on the previously mentioned data. As seen from Table V, the $a - b$ values remain constant within an accuracy of 40 millivolts. Using the values obtained for $a - b$ and the standard oxidation poten-

TABLE V. Metal Solubilities in their Trichloride Melts, Mole Fractions for M^{3+} and M^{2+} in Melts, Standard Oxidation Potentials of the M^{3+}/M^{2+} and M^{3+}/M^0 Couples, and the $a - b$ Calculated Values.

M	Solubilities of M in MCl_3 (Mol %)	M^{3+}	M^{2+}	$E^0_{M^{3+}/M^{2+}}$ (V)	$E^0_{M^{3+}/M^0}$ (V)	$a - b$ (V)[a]
Ce	9	0.73	0.27	−2.92	−2.33	0.48
Pr	19	0.43	0.57	−2.84	−2.34	0.50
Nd	30	0.10	0.90	−2.62	−2.32	0.44
Gd	5	0.85	0.15	−2.85	−2.28	0.39
Ho	20	0.40	0.60	−2.79	−2.37	0.43
Er	7	0.79	0.21	−2.87	−2.32	0.41
Pu	8	0.76	0.24	−2.59	−2.02	0.44

[a] Av. 0.44 ± 0.04; average value of the seven experiments and its average square deviation.

tials of $E^0_{M^{3+}/M^{2+}}$ and $E^0_{M^{3+}/M^0}$ we can calculate the MCl_2 mole fraction in the MCl_2–MCl_3 melt being in equilibrium with the metal for the lanthanides and actinides whose $E^0_{M^{3+}/M^{2+}}$ values are known. For $PmCl_2$, for example, this value was equivalent to 0.98, for $TbCl_2$ −0.27, for $CmCl_2$ −0.05, and for $BkCl_2$ −0.22. The M–MCl_3 phase diagrams for these elements are not available in the literature. Using the correlation found we can also solve a reverse problem, *i.e.* calculate the unknown value of $E^0_{La^{3+}/La^{2+}}$ (which turned to be equal to −2.95 V) based on the known solubility of a M in MCl_3 and its $E^0_{M^{3+}/M^0}$. At a later stage we proved these calculations experimentally. Our experimental value for the standard oxidation potential of the La^{3+}/La^{2+} couple is equal to -2.94 ± 0.08 V (5).

The established correlation between the standard oxidation potentials of the M^{3+}/M^{2+} and M^{3+}/M^0 couples and the metal solubility in its trichloride melt is realized irrespective of whether M^{2+} is present in the melt in an $f^nd^0s^0$ configuration (Pr, Nd, Pm, Sm, Eu, Dy, Ho, Er, Tm, Yb, Am, Bk, Cf, Es, Fm, Md, No [20]) or in an $f^{n-1}d^1s^0$ configuration (La, Ce, Gd, Tb, Pu, Cm [20]). Despite the fact that the lanthanide and actinide dichlorides apparently show different chemical properties in these two electrone states, the differences in the free energies of interaction with the respective chloride melts and water turn out to be the same. This enables us to plot a single scale of the standard oxidation potentials of the M^{3+}/M^{2+} couples which does not depend on the M^{2+} electron configuration and determine the connection between the metal solubility in its molten trichloride and the standard oxidation potentials of the M^{3+}/M^{2+} and M^{3+}/M^0 couples for aqueous solutions.

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