THERMAL STABILITY AND THERMODYNAMIC PROPERTIES OF TRISTETRAHYDROFURANATES LANTHANIDE BOROHYDRIDES

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Reliable data allows carrying out strict systems analysis, to determine modification regularities of physical and chemical properties of similar chemical compounds and to assess unknown properties of natural line members from periodic table.

The results of systematic investigations on study of thermal stability and thermodynamic properties determination of tristetra-hydrofuranates (THF) lanthanide borohydries (Ln) [1,2] are summarized in present work. Tensimetric methods with zero membrane – manometer, roentgen phase analysis (RFA) and chemical analysis are used.

Solvated lathanides borohydrides are obtained in result of exchange reaction between $NaBH_4$ and $LnCl_3$ in THF medium. The product is re-crystallized twice in THF medium and dried out in room temperature inside vacuum. According to chemical and RFA analysis, the product corresponds to the following formula: $Ln(BH_4)_3 \cdot 3THF$, where Ln – La, Nd, Sm, Gd, Er and Lu.

Tensimetric investigation carried out in equilibrium conditions has showed that balance in studied systems is reached by curing time of 150-160 hours of each figurative point on the curve of steam pressure dependence on temperature (barograms).

Desolvated process barograms of studied tristetrahydrofuranates of lanthanide borohydrides, presented as $LgP = f(10^3 / T)$ shows that in investigated temperature intervals the present dependence consists of two crossing direct lines. This indicates on two-stage character of desolvation process of studied compounds. The experimental data, processed by least-squares method with use of t-value of Student at 95-% confidence coefficient. Barogram equations of two stages of desolvation process are obtained (table 1).

Table 1. The values of equation coefficients of desolvation process stages $Ln(BH_4)_3 \cdot 3THF$.

Compound	$LgP_{ar \cdot THF}=B-A/T \cdot 10^3$			
	I stage		II stage	
	A	B	A	B
La	0,812	1,552	3,296	7,780
Nd	0,976	1,398	4,579	11,145
Sm	0,738	1,433	2,662	6,546
Gd	0,811	1,687	2,126	5,240
Er	0,940	1,642	3,373	8,420
Yb	1,185	2,732	3,486	8,758
Lu	1,370	2,944	1,878	4,449

According to the results of quantitative tensimetric experiments, it is determined that during the first process stage one THF mole is desolvated over temperature intervals 300…330 K according to the scheme

$$Ln(BH_4)_3 \cdot 3THF = Ln(BH_4)_3 \cdot 2THF + THF \quad (1)$$

and during the second stage remaining two THF moles are moved away in temperature intervals 340…380 K according to the scheme

$$Ln(BH_4)_3 \cdot 2THF = Ln(BH_4)_3 + 2THF. \quad (2)$$

According to equations (table 1) the thermodynamic properties of both desolvated process stages of studied tristetrahydrofuranates lanthanide borohydrides are calculated (table 2). On their basis, by the help of semi-empirical method which considers the impact of 4f-electrons number (Nf), contribution of spin (S) – and orbital (L) – angular momentums of trivalent lanthanide ions motions on properties (A) of studied compounds [3, 4], the thermodynamic properties of desolvated process stages of similar solvated borohydrides of whole lanthanide line are calculated by us (table 2).

Calculation is made by correlated equation

$$A_{Ln(BH4)3 \cdot 3THF} = A_{La(BH4)3 \cdot 3THF} + \alpha N_f + \beta S + \gamma' L_{(1-7)} \ (+ \gamma'' L_{(8-13)}) . \quad (3)$$

Values of equation coefficients (3) are presented in table 3.

Table 2. Thermodynamic properties of both stages of desolvation process $Ln(BH_4)_3 \cdot 3THF$.

Compounds	I desolvation stage				II desolvation stage			
	$\Delta H^0_T, \frac{kJ}{mol}$		$\Delta S^0_T, \frac{kJ}{mol \cdot K}$		$\Delta H^0_T, \frac{kJ}{mol}$		$\Delta S^0_T, \frac{kJ}{mol \cdot K}$	
	*	**	*	**	*	**	*	**
La	15,1	-	28	-	124	-	293	-
Ce	-	17	-	31	-	117	-	285
Pr	-	18	-	32	-	113	-	277
Nd	18,8	18	26	32	108	108	267	267
Pm	-	18	-	33	-	103	-	254
Sm	17,6	17	38	33	76	100	185	239
Eu	-	15	-	30	-	89	-	206
Gd	14,6	-	31	-	93	-	203	-
Tb	-	15	-	30	-	102	-	235
Ду	-	16	-	30	-	110	-	261
Ho	-	17	-	31	-	114	-	278
Er	18,0	18	31	34	129	116	322	286
Tm	-	19	-	38	-	114	-	286
Yb	20,5	19	46	43	103	107	259	269
Lu	20,9	-	50	-	104	-	261	-

-*- Experimental data

-**- calculated data

Table 3. Values of correlated equation coefficients.

Desolvation stages	Values	α	β	γ′	γ′′
I	ΔH^0_T	0.41	-0.97	0.54	-0.09
	S^0_T	1.52	-2.44	0.25	-1.51
II	ΔH^0_T	-1.47	-6.03	-0.17	3.07
	S^0_T	-2.24	-21.1	2.45	8.69

Obtained data allows carrying out of system analysis of thermodynamic characteristics of desolvation process of tris-THF borohydrides of whole lanthanide line.

The curves of thermodynamic characteristics changes of the first stage (equation 1) of desolvation process $Ln(BH_4)_3 \cdot 3THF$ dependence on lanthanide serial number are presented in Fig.1. Upper (a) and lower (b) curves are halved into separate parts with breaking at gadolinium. Accordingly [3,4] the slanting line, combining the point for Gd with appropriate points for La and Lu, determines contribution of spin quantum number (S).

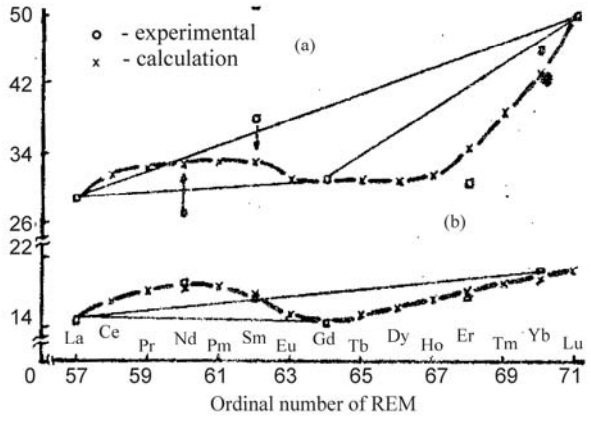

Fig. 1. Curves of entropy (a) and enthalpy (b) changes of first stage of borohydride desolvated process dependence from lanthanide serial number.

The point deviation with other lanthanide borohydride from these lines determines the contribution of orbital angular momentum (L).

Conclusions

Thus, on the basis of obtained values of thermodynamic values and step-by-step desolvation process character $Ln(BH_4)_3 \cdot 3THF$ it is possible to confirm:

- about conection nonequivalence between THF molecules and lanthanide borohydride;
- about demonstration (tetrad – effect) on curve of thermodynamic property of desolvation process of these compounds dependence on lanthanide serial number.

References

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