Synthesis of Gadolinium(III) Bromide and Modeling by the Experimental Design Method

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ABSTRACT: *In the present work, we have synthesized gadolinium(III) bromide, $GdBr_3$ from the gadolinium oxide, Gd_2O_3 by sintering brominating with ammonium bromide, NH_4Br. The influence of three main synthesis parameters (contact time, stoichiometry and temperature) on the reaction yield was studied and optimized. This study showed that the optimum conditions for the synthesis of $GdBr_3$ are the following: contact time t = 90 min, stoichiometry in moles (Gd_2O_3:NH_4Br = 1:18) and temperature T = 350 °C. The reaction yield for these parameters was equal to 97.27%. The modeling of our experiments results using a 2^3 full factorial design with six replicates at the center point gives us a first-degree model where it is clear that the reaction yield is a function of these three parameters.*

KEYWORDS: *Gadolinium(III) bromide; lanthanide halides; Reaction yield; 2^3 full factorial design.*

INTRODUCTION

Lanthanide bromides and iodides are attractive components for doses in high-intensity discharge lamps [1] and new highly efficient light sources with energy saving features [2]. When combined with other metal halides, they offer the opportunity to design light sources with high efficacy and good color rendition. Photoluminescence and photostimulated luminescence of lanthanide-doped bromide materials induced recently active research targeted to commercial X-ray storage phosphors [3]. There is also a continued interest in the search for new scintillators for the detection of radiation [4-7]. Lanthanide trihalides LnX_3, (pseudo)-elpasolites M_2ALnX_6, and ternary halides $A_mLn_nX_o$ have been investigated recently in this respect [6]. These different applications require knowledge of their physicochemical, structural and thermodynamic properties. The study of these properties requires high purity of these salts in order to have accurate data [8-10]. The synthesis of lanthanide trihalides LnX_3 is the preliminary step to make. The synthesis parameters of lanthanide halides

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(temperature, contact time, chemical composition...) therefore remain to be determined according to the nature of the lanthanide [11, 12].

The present work is focused on $GdBr_3$ synthesis by sintering brominating gadolinium oxide with ammonium bromide. It reports the influence of three main synthesis parameters (contact time, stoichiometry and temperature) on the reaction yield. The optimum conditions for synthesis of gadolinium(III) bromide were thus determined and discussed. A full factorial design was used in order to determine a mathematical model connecting these three factors with reaction yield and to gain insight into how the various factors interact and influence the response.

EXPERIMENTAL SECTION

Gadolinium(III) bromide, $GdBr_3$ was synthesized from the gadolinium oxide, Gd_2O_3 (Sigma-Aldrich, 99.9%) by sintering brominating with ammonium bromide, NH_4Br (Sigma-Aldrich, 99%). Gadolinium oxide Gd_2O_3 and ammonium bromide NH_4Br in well-defined proportions were homogenized in mortar and placed in an alumina crucible.

The crucible with reaction charge was introduced into a quartz reactor and maintained under argon. The assembly was housed in a Nabertherm tubular furnace RT 50-250/11 programmed at a desired temperature. The maintenance of the experimental enclosure under a purified argon atmosphere is necessary. The pressure and the flow rate of argon circulating in the reaction chamber are well controlled, in order to chase the volatile products resulting from the reaction (NH_3, HBr,...). Gaseous circuits are connected via the valves of the argon bottle to the quartz reactor. Two ampoules, containing acidic and basic solutions, respectively, are connected to the quartz reactor to trap the volatile products. At the end of each reaction, the synthesized product in solid form was dissolved in a solution of HCl (0.05 N) with magnetic stirring and the solution is then filtered using a vacuum pump. Dissolution of the product takes place in diluted solution of HCl in order to find the amount of $GdBr_3$ formed during the process and to avoid the formation of $Gd(OH)_3$ hydroxides. 10 ml of the solution are taken, to which is added 10 ml of a buffered solution at pH = 5.6 (CH_3COOH/CH_3COONa) and heated to 80 °C for chemical analysis. The chemical analysis of the synthesized gadolinium(III) bromiode, $GdBr_3$ was performed by a complexometric titration with standard EDTA solution, using xylenol orange as indicator. The details of the preparation procedure were presented previously [12].

RESULTS AND DISCUSSION

Thermodynamic study of the reaction

Beforehand a thermodynamic approach was carried out to study the feasibility of the synthesis reaction. It allows the determination of standard thermodynamic parameters such as enthalpy, entropy and Gibbs free energy of reaction.

The synthesis of gadolinium(III) bromide, $GdBr_3$, from gadolinium oxide, Gd_2O_3 by sintering brominating with ammonium bromide, NH_4Br can be described by the balanced equation:

$$Gd_2O_3(s) + 6NH_4Br(s,g) \rightarrow 2GdBr_3(s) + 6NH_3(g) + 3H_2O(\ell,g) \quad (1)$$

Using thermodynamic data found in literature [13, 14], we have calculated the thermodynamic quantities for the standard enthalpy of reaction, the entropy of reaction and standard Gibbs free energy of reaction. These quantities are also calculated according the temperature.

The results of the above calculation are presented in Fig. 1.

Fig. 1a shows that the reaction enthalpy is positive between room temperature and T = 606 K (sublimation temperature of NH_4Br) over the entire temperature range used. The enthalpic jump observed at 373 K is related to the vaporization of water and the reaction remains endothermic in this temperature range.

The entropic contribution is quite significant (Fig. 1b). This is expected since the reaction is accompanied by a substantial disorder linked to the release of gaseous products (increasing number of moles of gas).

The Gibbs free energy of reaction as a function of the temperature was calculated according to the equation:

$$\Delta_r G_T^0 = \Delta_r H_T^0 - T\Delta_r S_T^0 \quad (2)$$

The enthalpic and entropic contribution lead to a decrease in the Gibbs free energy of reaction with temperature (Fig. 1c). So the increase in temperature

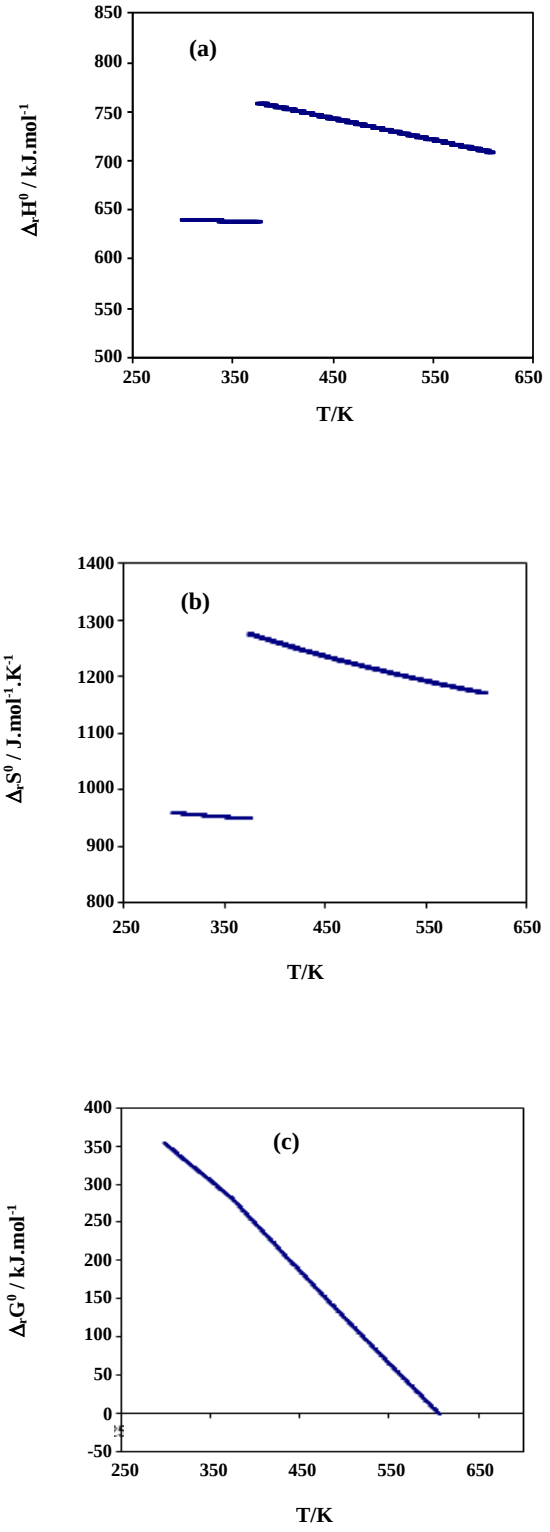

Fig. 1: Thermodynamic functions: (a) Standard enthalpy of reaction, (b) Standard entropy of reaction, and (c) Standard Gibbs free energy of reaction.

promotes the synthesis of gadolinium(III) bromide. Graphically we can deduce an inversion temperature T = 606 K, beyond which the reaction is favorable.

Determination and optimization of the synthesis parameters

In this work, we studied the influence of three synthesis parameters (contact time, stoichiometry and temperature) on the reaction yield.

The reaction yield, denoted R, was calculated using the equation*:*

$$R = \frac{Mass\ of\ product\ obtained}{Theoretical\ mass\ of\ product}\ x\ 100 \qquad (3)$$

The mass of product obtained is the mass of $GdBr_3$ synthesized. Theoretical mass of product is the mass corresponding to a yield of 100 % calculated from the mass of the gadolinium oxide.

The experimental results for the influence of each synthesis parameters on the reaction yield are graphically represented in Fig. 2. In each experiment, one parameter is varied while keeping the other two parameters constant.

From the results, we observe an increase of the reaction yield R (%) and stabilization beyond 90 min (Fig. 2a), molar ratio Gd_2O_3:NH_4Br = 1:18 (Fig. 2b), and 350 °C (Fig. 2c), respectively.

Taking into account these observations, we can conclude that the optimum conditions for synthesis of gadolinium(III) bromide are: contact time t = 90 min, stoichiometry in moles Gd_2O_3: NH_4Br = 1:18 and temperature T = 350 °C. Under these conditions, the reaction yield reached 97.27%.

Modeling by the experimental design method

The experimental design method is a statistical axis that allows the modeling of a random phenomenon with the aid of a minimum number of tests. It is increasingly used in industry because it allows to better organize the tests that accompany scientific research or industrial studies. In this work, we have applied the experimental design method to model the reaction yield depending on the three factors (contact time, stoichiometry and temperature). This method allows us to find a mathematical model that links the reaction yield

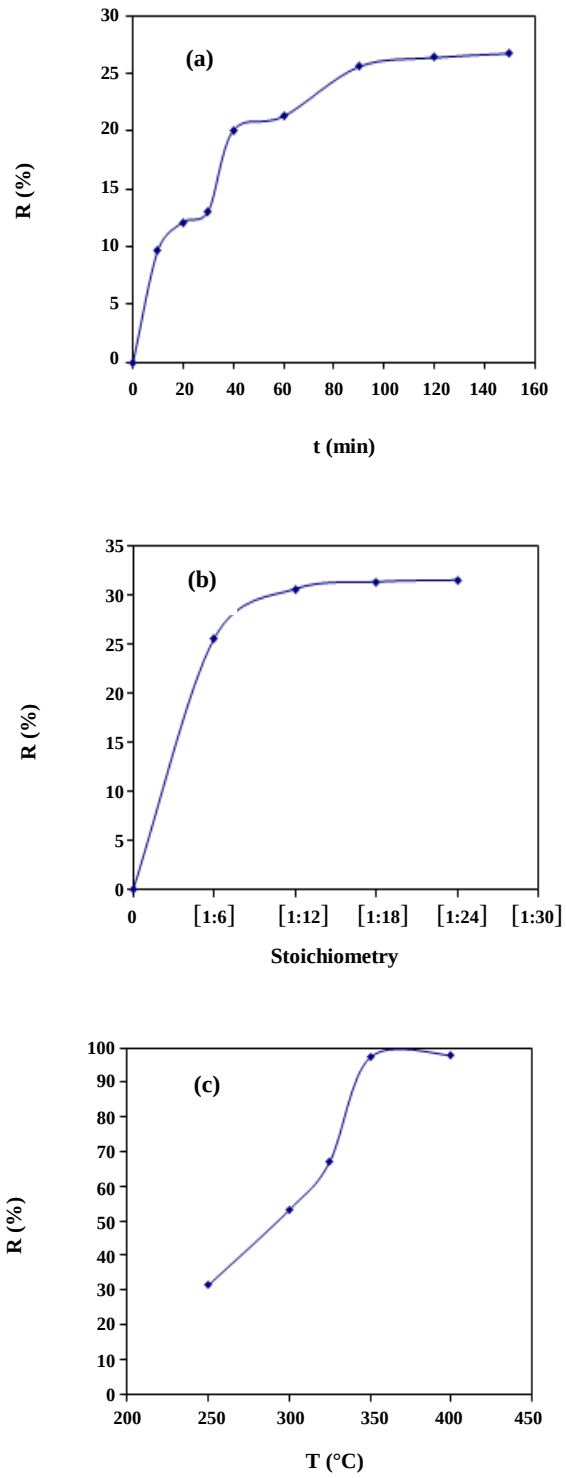

Fig. 2: Influence of synthesis parameters on the reaction yield R (%): (a) contact time (molar ratio Gd_2O_3:NH_4Br = 1:6 and T = 250 °C), (b) stoichiometry (t = 90 min and T = 250 °C), and (c) temperature (t = 90 min and molar ratio Gd_2O_3:NH_4Br = 1:18).

to the three factors, and allows us to examine the main effects and the interaction effects of three factors on the reaction yield. A full factorial design of 2^3, with 6 experiments at the central point and therefore 14 experiments in total, were used to evaluate the effect of the three factors. The replication of experiments at the central point was made in order to evaluate the standard deviation of each parameter and to detect if there is an inflection point. The high (+1), center (0) and low (−1) levels defined for the 2^3 factorial designs were summarized in Table 1. The lowand high levels of the factors were selected according to the optimization results.

The coded values of x_j were obtained from the following relationship ([15,16]):

$$x_j = \frac{z_j - z_j^0}{\Delta z_j}, \quad j = 1, 2, 3 \qquad (4)$$

Where: $z_j^0 = \frac{z_{j\max} + z_{j\min}}{2}$ (5) and

$$\Delta z_j = \frac{z_{j\max} - z_{j\min}}{2} \qquad (6)$$

x_j is the coded value of z_j, z_j^0 is the value of z_j at the central point of the investigation domain and Δz_j is the step size, $z_{j\max}$ and $z_{j\min}$ represent the maximum and the minimum level of factor j in natural units, respectively. Table 2 regroups the results for the design matrix obtained from the 14 experiments.

A first-order mathematical model was chosen to fit the experimental:

$$\hat{R} = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{123}x_1x_2x_3 \qquad (7)$$

Where $\hat{R}$ is the predicted reaction yield, b_0 is the global mean and b_j represents the other regression coefficients.

The coefficients (b_j) of the regression equation are estimated by the relation:

$$b = \left(X^tX\right)^{-1} X^t R = X^{-1}R \qquad (8)$$

With:

X: the matrix effects defined in Table 2

X^t: the transposed matrix of effect

Table 1: Values of the factors at different levels.

Factors		Low level	Center level	High level
Real factors	Coded levels	−1	0	+1
z_1 : Time (min)	x_1	10	50	90
z_2 : Stoichiometry in moles (Gd_2O_3: NH_4Br)	x_2	1:6	1:12	1:18
z_3 : Temperature (°C)	x_3	250	300	350

Table 2: Design matrix and the results of the 2^3 full factorial design.

Experiments	Experiment's matrix code			Real experimental plan			Measured response
	x_1	x_2	x_3	t (min)	Gd_2O_3:NH_4Br	T (°C)	*R* (%)
1	-1	-1	-1	10	1:6	250	9.75
2	1	-1	-1	90	1:6	250	25.56
3	-1	1	-1	10	1:18	250	24.11
4	1	1	-1	90	1:18	250	31.36
5	-1	-1	1	10	1:6	350	25.35
6	1	-1	1	90	1:6	350	80.66
7	-1	1	1	10	1:18	350	28.25
8	1	1	1	90	1:18	350	97.27
9	0	0	0	50	1:12	300	32.26
10	0	0	0	50	1:12	300	32.99
11	0	0	0	50	1:12	300	32.26
12	0	0	0	50	1:12	300	31.72
13	0	0	0	50	1:12	300	32.44
14	0	0	0	50	1:12	300	32.08

R: the matrix of responses

The values of the coefficients estimated are summarized in Table 3

Statistical analysis

Checking the significance of the coefficients: STUDENT test

The Student's test is given for each effect by:

$$t_j = \frac{|b_j|}{S_{bj}} \tag{9}$$

Where:

$$S_{bj} = \frac{S_{rep}}{\sqrt{N}} \tag{10}$$

$$S_{rep}^2 = \frac{\sum_{i=1}^{n_0} \left(R_{0i} - \overline{R}_0\right)^2}{n_0 - 1} \tag{11}$$

$$\overline{R}_0 = \frac{\sum_{i=1}^{n_0} R_{0_i}}{n_0} \tag{12}$$

S_{rep}^2 : is the reproduction variance, and S_{bj} : is the root-mean-square deviation.

b_j : coefficient, N: number of experiments (N = 8), n_0 : number of experiments at the central point (n_0 = 6), R_{0_i} : observed value of reaction yield at the *i* central point, and $\overline{R}_0$ is the mean reaction yield at the central point.

Table 3: Values of the model's coefficients

b_0	b_1	b_2	b_3	b_{12}	b_{13}	b_{23}	b_{123}
40.29	18.42	4.95	17.59	0.64	12.66	-0.08	2.78

Table 4: Coefficients t_j of the STUDENT test.

t_0	t_1	t_2	t_3	t_{12}	t_{13}	t_{23}	t_{123}
271.388	124.1	33.412	118.491	4.311	85.281	-0.539	18.727

The set of coefficients t_j of the STUDENT test calculated are gathered in Table 4.

The tabulated value of STUDENT $((N, n_0 - 1),\ t_{0.05})$, is found equal to 2.57. From the results, the value t_{23} = -0.539 is less than the tabulated value. The corresponding coefficient b_{23} is excluded therefore from the regression equation. The linear model subject to validity is written according to the following equation:

$$\hat{R} = 40.29x_0 + 18.42x_1 + 4.95x_2 + 17.59x_3 + 0.64x_1x_2 + 12.66x_1x_3 + 2.78x_1x_2x_3 \quad (13)$$

Validation of the model: FISHER test

a) Bias search

No bias can be verified by Fisher's test. The F-test is given by:

$$F = \frac{S_{res}^2}{S_{rep}^2} \quad (14)$$

Where S_{res}^2 is the residual variance:

$$S_{res}^2 = \frac{\sum_{i=1}^{N}\left(R_i - \hat{R}_i\right)^2}{N - \lambda} \quad (15)$$

λ : number of the significance parameter in the regression equation (here it is equal to 7).

$\hat{R}_i$: is the calculated value of the response for the i experiment.

The calculated F-value for this model is equal to 0.3025. The tabulated $F(0.95, N - \lambda, n_0 - 1)$= 6.61 was greater than the calculated value. Equation (13) can be considered as adequate and the model is unbiased.

b) Validation of the regression equation

The validity of the regression equation is based on the statistical Fisher's test. The F-value is calculated by the following equation:

$$F = \frac{\sum_{i=1}^{N}\left(\hat{R}_i - \overline{R}\right)^2 / (\lambda - 1)}{\sum_{i=1}^{N}\left(R_i - \hat{R}_i\right)^2 / (N - \lambda)} \quad (16)$$

The calculated *F*-value for reaction yield " F = 21043.52 " is much greater than the tabulated $F(0.95, \lambda - 1, N - \lambda)$= 234 ; we can conclude that the regression equation is thus very significant on the response, and the adjustment of the model is adequate.

Correlation coefficients

The correlation coefficient is defined by:

$$R^2 = \frac{\sum_{i=1}^{N}\left(\hat{R}_i - \overline{R}\right)^2}{\sum_{i=1}^{N}\left(R_i - \overline{R}\right)^2} \quad (17)$$

The correlation coefficient R^2 was found to be 0.9997.

Since our sample size is not very large, it is necessary to make a correction for the systematic error [17]. The corrected coefficient is calculated according to the equation:

$$R^2_{Corr} = R^2 - (1 - R^2)\frac{\lambda - 1}{N - \lambda} \quad (18)$$

The corrected coefficient R^2_{Corr} was found to be 0.9976.

The value is close to 1. The model allows to correctly represent the experimental results.

Residual analysis

Quality assessment of the first-degree model can be done by residual analysis. This test consists of analyzing

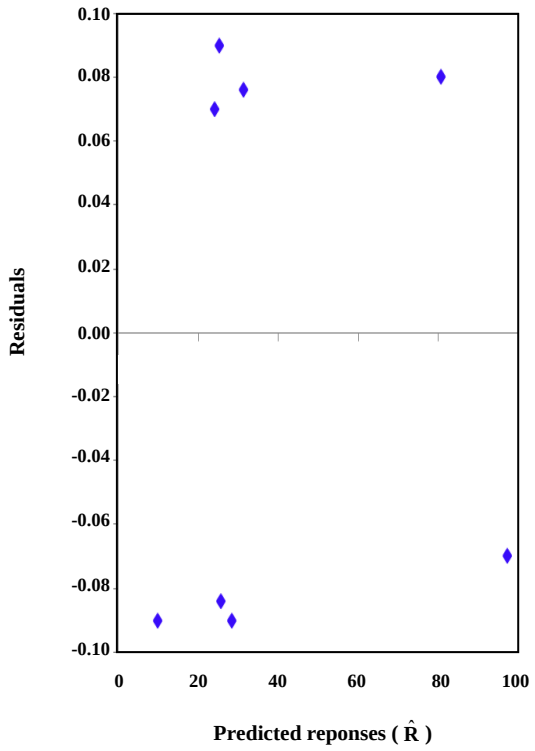

Fig. 3: Diagram of residues

the plot of observed residues depending on the predicted responses [18, 19]. The calculation of the residues is given by the difference between the values of the experimental responses and those predicted by the model according to the following equation:

$$Residus = \varepsilon = \left(R_i - \hat{R}_i\right) \quad (19)$$

Residue values are plotted according to the predicted responses in Fig. 3.

The graph shows a random distribution of points; which confirms the absence of a relationship between predicted responses and residues. Therefore, the first-degree model (13) that we have established explains well the experimental results.

Study of main effects and interaction effects

Study of main effects

The effect of a factor on the response is evaluated by the variation of the response when the factor goes from the low level to the high level. The effects of the three factors (contact time, stoichiometry and temperature) on the response are shown in Fig. 4.

Fig. 4 shows that an increase in contact time (a), stoichiometry (b), temperature (c), from low to high levels resulted in an increase in the reaction yield R (%). This indicates that all factors have a positive effect on the response [20, 21]. In addition, we can see that the effects of contact time and temperature on the response are very significant.

Study of interaction effects

The interaction effect is relative to the combined influence of two different factors on the response. There is an interaction when the effect of one factor on the response depends on the level of the other factor. An interaction between two factors is significant, if the lines of the effects are not parallel [22, 23].The interactions effects between factors are shown in Fig. 5.

Fig. 5 (a) shows a strong interaction between contact time and temperature. In addition, the effect of contact time is greater when the temperature is high. However, the interaction between contact time and stoichiometry (Fig. 5 b), as well as between stoichiometry and temperature (Fig. 5 c), is neglected (the lines are almost parallel).

These results confirm that the simultaneous control of the contact time and temperature plays a major role in the synthesis of $GdBr_3$.

Response surfaces and isoreponses curves

To get an overview of the results, we plot the response surfaces and isoreponses curves. Fig. 6 shows the evolution of the reaction yield R (%) as a function of (a) contact time and temperature (molar ratio Gd_2O_3:NH_4Br = 1:18), (b) contact time and stoichiometry (T = 350 °C), and (c) temperature and stoichiometry (t = 90 min).

The response surface plot allows delimiting zones of interest for the reaction yield and shows that all factors have a positive effect. The high reaction yields (> 80%) represented by the red color are located particularly in zones of high temperatures and high contact times.

The corresponding isoreponses curves allows to visualize the optimum conditions and to determine the best yield for three factors when a factor has been fixed. We can thus extract directly from these graphs the estimated value of the desired yield R (%) at any point in the field of study.

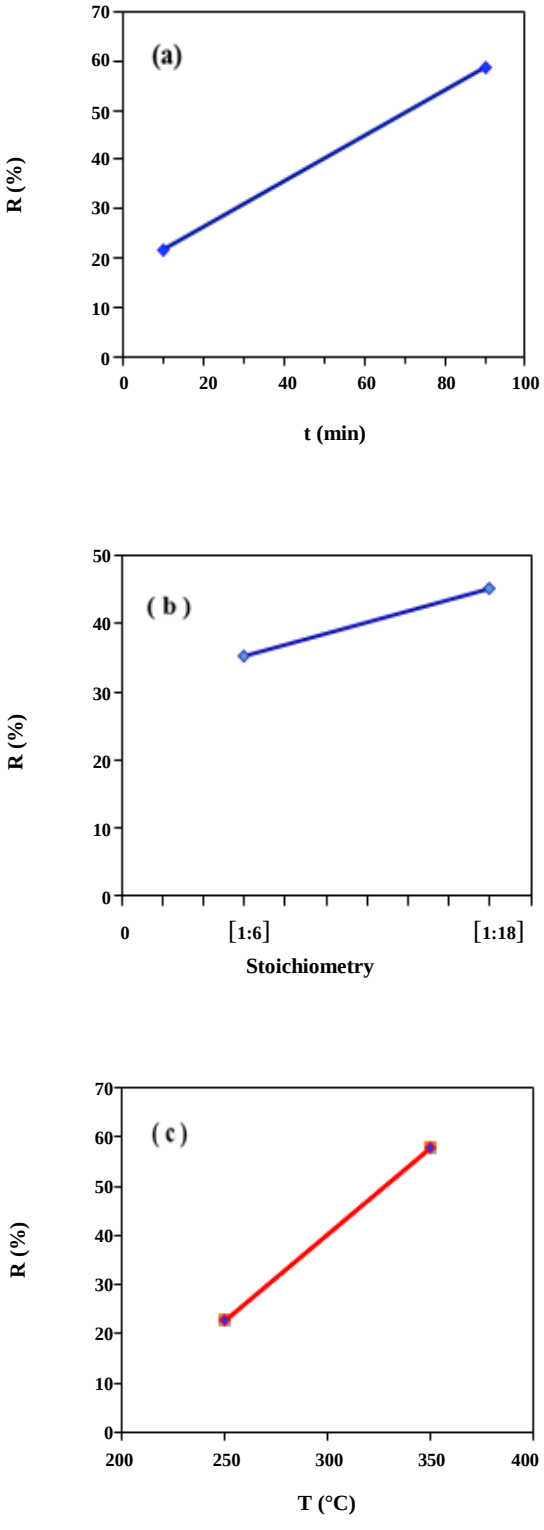

Fig. 4: Main effects plot for reaction yield R (%): (a) contact time, (b) stoichiometry, and (c) temperature.

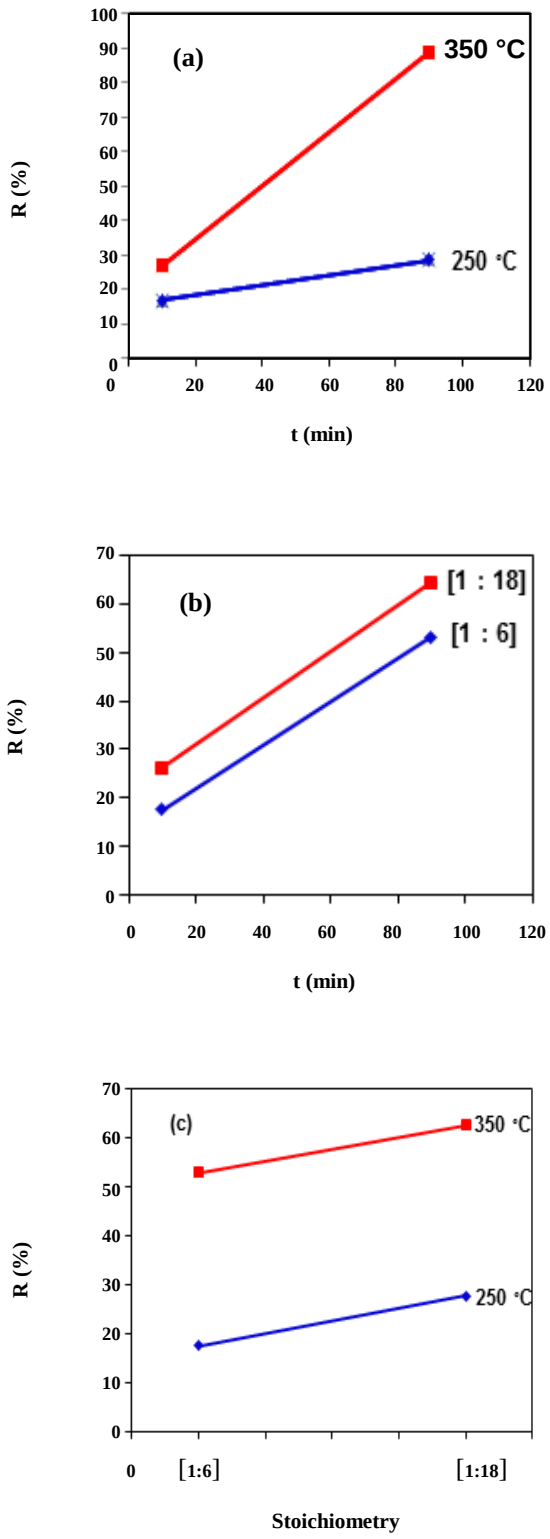

Fig. 5: Interaction effects plot: (a) time/temperature, (b) time/stoichiometry, and (c) stoichiometry/temperature.

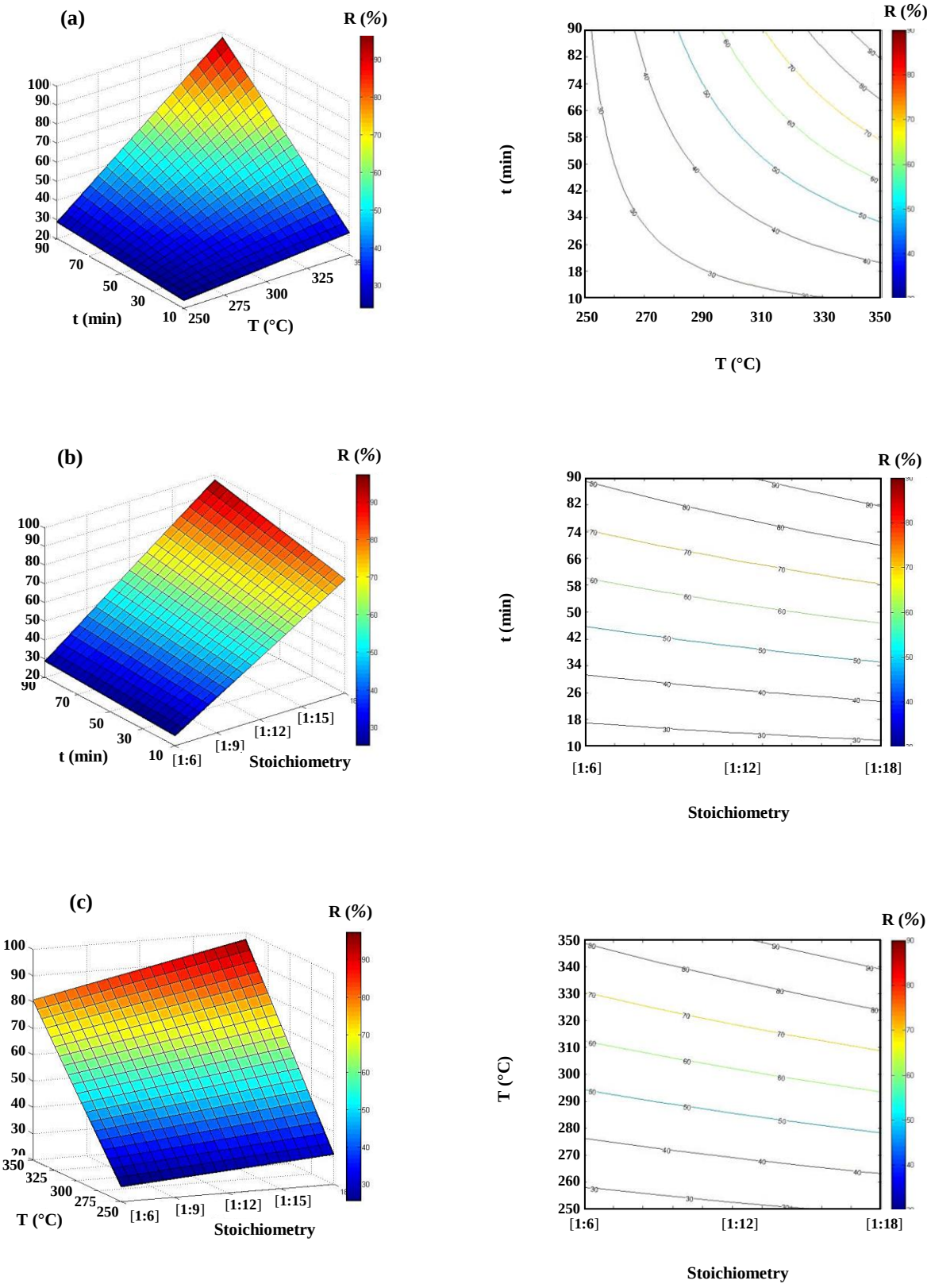

Fig. 6: Response surfaces and isoreponses curves of the reaction yield R (%) as a function of (a) contact time and temperature (molar ratio Gd_2O_3:NH_4Br = 1:18), (b) contact time and stoichiometry (T = 350 °C), and (c) temperature and stoichiometry (t = 90 min).

The isoreponses curves indicate a non-linear relationship between contact time and temperature (Fig. 6 a). These results confirms a strong interaction between contact time and temperature.

CONCLUSIONS

The study of the influence of three main synthesis parameters on the reaction yield shows that the optimum conditions for synthesis of gadolinium(III) bromide are: contact time t = 90 min, stoichiometry in moles Gd_2O_3: NH_4Br = 1:18 and temperature T = 350 °C. Under these conditions, the reaction yield reached 97.27%.

Modeling the yield of the $GdBr_3$ synthesis reaction by a 2^3 -full factorial design resulted in a first-order mathematical model. The analysis of the model showed that the three factors have a positive influence on the reaction yield and it showed the existence of significant interactions between the contact time and temperature. The validity of this study was limited to, contact time between 10 and 90 min, stoichiometry between 1:6 and 1:18 and temperatures between 250 and 350 °C.

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