

INFLUENCE OF TEMPERATURE AND CONCENTRATION OF WATER ON LANTHANUM NITRATE DISSOLUTION AND CRYSTALLIZATION

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Abstract

The curves of heating and cooling crystalline lanthanum nitrate were registered and numerical differentiation was carried out. The first derivatives of kinetic curves expressed as the temperature function make it possible to carry out comparative studies of dissolution and crystallization. Superposition of relative water concentration scale on the third derivative of heating and cooling curves make the analysis of stoichiometry and mechanism of hydration changes possible in the solid phase and saturated solutions.

Keywords: numerical differentiation, relative water concentration, thermal analysis, thermal spectrum

Introduction

In the polythermal processes of hydrated ionic salts heating, rapid boiling of the formed liquid (alloy) takes place. This promotes the change of spatial configuration of hydrated ions and, as a consequence, leads to an uncontrolled mechanism of decomposition and formation of serious quantitative errors in the thermal analysis. In earlier studies [1] some attempt were made to overcome the above difficulties. The main idea consists in the registration of temperature changes during the polythermal heating as well as in polythermal crystallization and numerical treatment of the obtained heating and cooling curves [2].

Experimental

Lanthanum nitrate (LaNO_3)₃·5.9740H₂O) was obtained by means of polythermal crystallization from water. The samples of 80.0 g crystals were put to a microreactor with the water jacket and increasing amounts (2.0–20.0 cm³) of redistilled water were introduced. The resulting mixture was heated to 42.92–97.71°C (Figs 1 and 2) by hot water from the thermostat. Changes of temperature during dissolution and crystallization of the solid phase were recorded with 10 or 60 s sampling time and with

0.01°C accuracy, by means of the measuring instrument CX-721 (Elmetron, Poland) with the temperature sensor PT-100. Crystallization took place due to mechanical stirring and spontaneous cooling to 13.03–60.3°C (Figs 1 and 2) in air after introducing seeds into the hot supersaturated solution.

The numerical differentiation and interpolation with the use of the natural spline function were carried out using the PSI-Plot program (Poly Software Int.). Relative concentration of water R was the number of moles of water per 1 mole of $\text{La}(\text{NO}_3)_3$.

Results

The kinetic curves of heating and cooling for the systems of the lowest water concentration and with 10 s sampling time are presented in Fig. 1a and their first derivatives as the temperature function in Fig. 1 (bic).

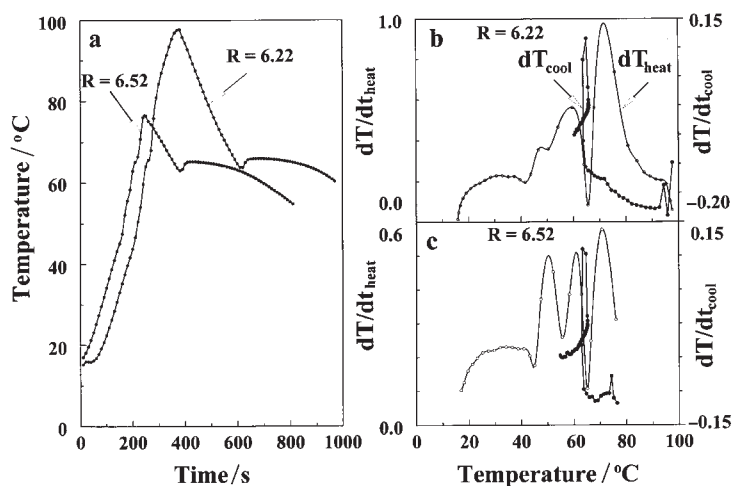


Fig. 1 Heating and cooling curves for the systems of lowest water concentration (a); the first derivatives of heating (dT_{heat}) and cooling (dT_{cool}) curves as the temperature function (b, c)

The deep minimum of the first derivative of the heating curve (dT_{heat}) overlaps the initial section of the loop of the first derivative of the cooling curve (dT_{cool}).

Data in Fig. 2 indicate that the minima of dissolution along with the crystallization maxima (loops) of the first derivatives shift to lower temperatures with increasing the water concentration.

The deep minimum of each function dT_{heat} possesses a high peak on the right side. The section of function dT_{heat} between the minimum and maximum of dissolution corresponding to the area of saturated solution shows the energetic end of dissolution and at the same time constitutes a post-dissolution period of dissolution. A further increase of water concentration in the crystalline systems leads to disconnection of lower temperature sections of the function dT_{heat} but the left and right sides of dissolution minimum become larger and overlap a greater number of low amplitude

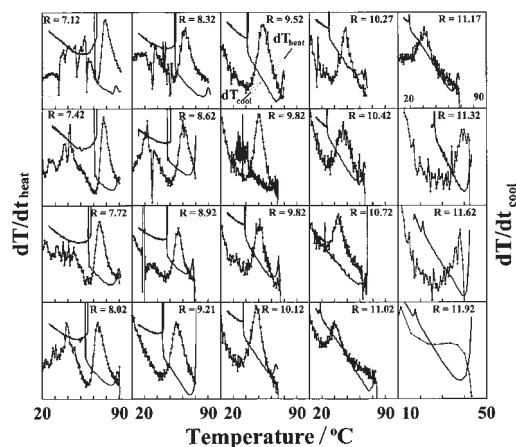


Fig. 2 First derivatives of the heating and cooling curves of the crystalline systems under investigation as the temperature function

peaks. With high water concentration the dissolution minima along with right and left sided maxima become shallow and flat leading even to the loss of left sided dissolution maximum like in the system of the concentration $R=11.17$.

The first derivatives of cooling curves (Figs 1 and 2) possess deep minima on both sides of the highest crystallization maximum. The right sided minimum indicates the end of losing the thermal momentum obtained by the system in the heating (dissolution) process and the left sided minimum indicates the end of post-crystallization period of polythermal crystallization. In the post-crystallization period the growth of crystalline phase was under the influence of the heat evolved during the crystalline phase formation.

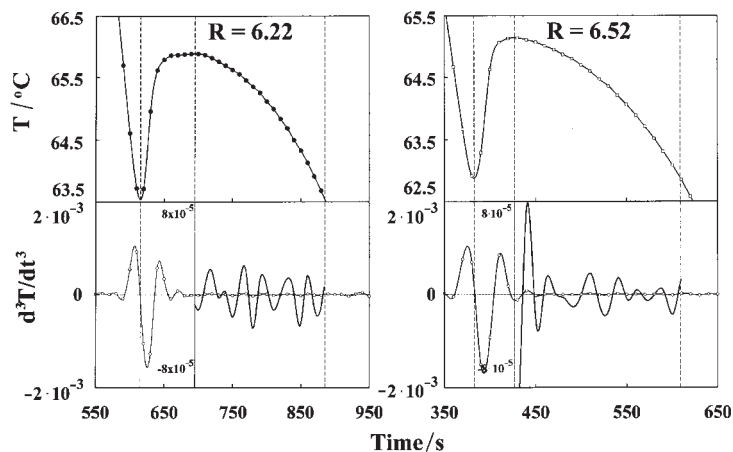


Fig. 3 Section of the cooling curve with its third derivative (d^3T/dt^3) for the system of lowest water concentration

As follows from Fig. 3 with the relative water concentration $R=6.22$ and 6.52 a rapid increase of temperature by 2.35 and 2.26°C respectively takes place in the cooling process. Reaching the temperature like that before the phase change closes the loop of the function dT_{heat} . The temperature loop area as shown in Fig. 3 becomes reduced with the increase of water in the crystallization systems.

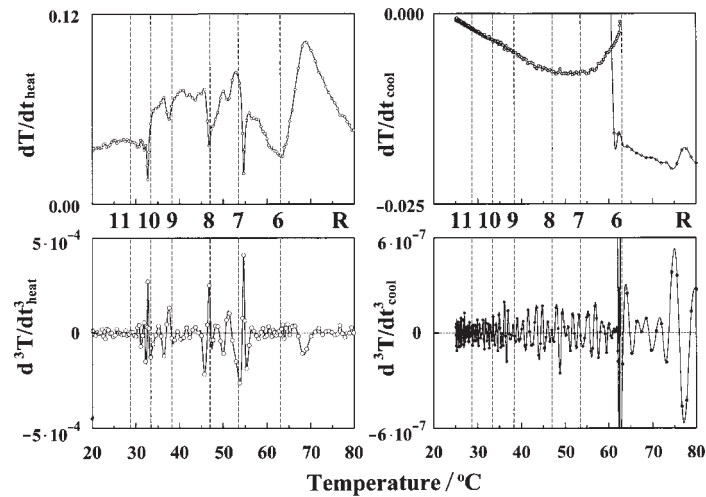


Fig. 4 First and third derivatives of the heating and cooling curves as the temperature function with the marked scale for the crystallization system of $R=7.12$

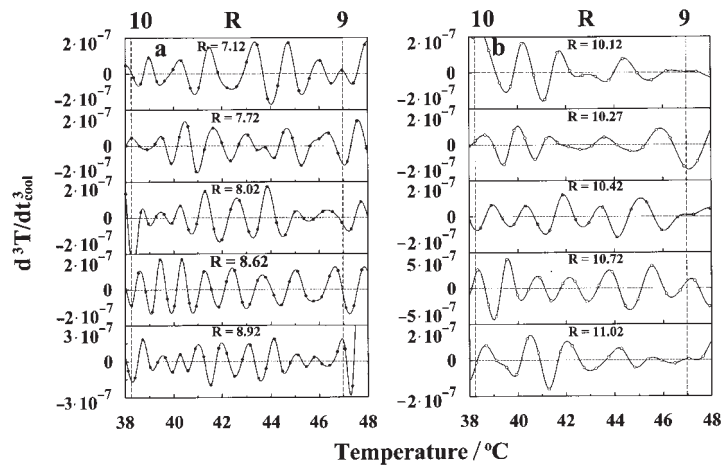


Fig. 5 Third derivative of cooling curves as the temperature function and in the range of elementary water concentration ($R=9-10$) for the crystallization systems of increasing water concentration: a – for the crystalline phase growth; b – for the saturated solutions

The data in Fig. 4 indicate that the maxima and minima of the dT_{heat} and dT_{cool} functions correspond to the minima and maxima of their third derivative. Superposition of the relative water concentration scale obtained by solubility polytherm [3] on the third derivative function shows that between total values of water concentration there can be found minima and maxima of the third derivative function whose number increases with the increase of water concentration and the decrease of crystallization or dissolution temperature.

Moreover, it follows from Fig. 5 that the minima and maxima of the function d^3T_{cool} in the elementary range of relative water concentration e.g. $R=9-10$, characterizing hydration equilibria and phase transition in the saturated solution and during the growth of crystalline phase are superimposed, phase shifted, new ones of incomplete (four-phase) exothermic and endothermic cycles disappear or appear [4].

Discussion

The above presented data indicate that thermal behaviour of lanthanum nitrate during polythermal dissolution and crystallization depends significantly on water concentration. Small batches of water introduced into the crystallization system dissolve a part of crystalline phase leading to simplification of the third derivative spectrum. At the same time the increasing amount of the saturated solution improves the contact with temperature sensor and disconnection of low temperature sections of the first derivatives of the heating curves. High amplitudes of the function dT_{heat} compared with the function dT_{cool} were a result of tenfold larger rate of heat supply into the system during dissolution than its carrying away during crystallization. Therefore the polythermal heating and cooling processes under the conditions of optimal water (solvent) concentration, verified rate of temperature changes, good contact of the crystalline phase with the temperature sensor and other well defined measurement conditions, can be a simple and convenient way of hydrated crystalline phases thermal analysis.

With the increases of water concentration, the function dT_{heat} was largely shaped by low-energetic hydration changes. As a result, diffusion resistance by the crystalline phase became weaker. Thus superposition of hydration equilibria in the crystalline phase and the saturated solution was observed. Their incomplete superposition resulted mainly from kinetics of supplying and carrying away heat leading to thermal supersaturation caused by relaxation occurring both in the crystalline phase and the saturated (concentrated) solutions.

Shape of kinetic curves obtained in the heating and cooling processes depends mainly on the thermal potential between the system under investigation and the surrounding: the positive one in the case of dissolution and the negative one during crystallization. Therefore the two-phase shift between the functions dT_{heat} and dT_{cool} and the mirror reflection symmetry towards the temperature axis is a natural consequence of heat flow direction.

Occurrence of one well shaped minimum of the third derivative among the total values R indicates hydration change with one water molecule participation. A great

number of minima among the elementary values R points out that the mechanism of substitution or introduction of one water molecule into the hydration sphere of lanthanum ion is of several stages and includes a large set of molecules (clusters) of lanthanum nitrate.

Conclusions

- The numerical analysis of the first and third derivatives of heating and cooling curves obtained at the changing concentration of water in the crystalline systems is a simple and convenient way to carry out comparative studies on equilibria and hydration changes in the crystalline phase and the concentrated solutions.
- The process of polythermal dissolution and crystallization is mutually diphasic shifted and includes both post-dissolution and post-crystallization periods.
- Phase shift, shape and size of interpolation loops of the third derivative of heating and cooling curves are determined by water concentration, kinetics of heat supply and carrying away from the system under examination as well as by instability of measurement conditions.
- Superposition of water concentration scale on the functions of third derivative of heating and cooling curves makes the studies of stoichiometry and hydration change mechanism possible in the solid phase and saturated solutions.

References

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