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Influence of temperature on the hydration equilibria
and phase transitions. II. Polythermal dissolution
of La(NO₃)₃ · 2NH₄NO₃ · 4H₂O from water

Wpływ temperatury na równowagi i przemiany hydratacyjne.
II. Politermiczne rozpuszczanie La(NO₃)₃ · 2NH₄NO₃ · 4H₂O

1. INTRODUCTION

From the previous investigations [1] it results that the temperature changes in the process of polythermal crystallization registrated in a longer time interval may be useful for analysis of low-energetic hydration equilibria and hydration transitions. In this work the efforts are made to analyze the effect of temperature and concentration of solvent on the dissolution process of lanthanium-ammonium nitrate in water based on the numerical analysis of heating curves obtained from the polythermal dissolution and thermal dehydration. Because the dissolution of crystallic phase is an integral element of the fractional crystallization (recrystallization), therefore the knowledge of material-energetic balance of this process [2] can give complete optimisation of periodical and counter-current and espectially continuous method of separation and purification of ionic substances by crystallization [3]. The possibility of precise registration of little changes of temperature and its extension in numerical differentiation creates conditions to study the influence of thermal dehydration on the quality and applicability of the product obtained by drying and/or thermal decomposition.

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2. EXPERIMENTAL

Lanthanium-ammonium nitrate from the same production charge [1] were used in experiments. For dissolution of each preparation sample there were used various amounts of redistilled water, next registering the changes of temperature every 10 seconds according to the procedure described in the previous paper [1]. Variable heating rate was obtained owing to the filling of thermostat with water having different temperature at the moment of beginning of the tested system heating. Derivatographic measurements were made on a Q-1500D derivatograph with a Derill countershaft at a heating rate of $0.0224 \deg \cdot \sec^{-1}$ and with 12sec of sampler time.

3. RESULTS AND DISCUSSION

Heating curves of the tested crystallization systems of different concentration of water (R_0), Table 1, against the background of their first derivatives are presented in Figure 1. For systems XVII–XX, the same amount of water was used for dissolution of the sample ($R_0 = 7.8652$).

Each heating curve as well as its first derivative are characterized by non-monotonous course. This non-monotony becomes more and more distinct as the concentration of water in the system decreases. On the plots of the first derivatives there can be distinguished two sharp maxima, which divide each of the heating curves into three sections. First section is connected with the process of getting heat from the exterior which is equivalent to the heat of crystallic phase hydratation by water introduced to the system, the second section, between the maxima, illustrates thermal decomposition of the undissolved part of crystallic phase in water ended with its molting, the third section is formed by the heating process of the salt saturated water solution.

The temperature and time of appearance of the first derivative second maximum and its final temperature of dissolution (T_S) together with the three maxima localized on the left and right sides of this maximum were determined by the interpolation method based on the appropriate minima of the third derivative and listed in Tables 2 and 3, respectively. In Figure 2 there is plotted the temperature of T_S and initial crystallization temperature (T_0) [1] as the functions of relative concentration of water (R_0). The parallelism of the courses of R_0 *vs.* T_0 and R_0 *vs.* T_S is confirmed by the slope of two straight lines obtained by approximation made by the least square method (Tab. 4).

Table 1. Some parameters of polythermal dissolution of lanthanum-ammonium nitrate
in water. System (0) – derivatographic data
Niektóre parametry politermicznego rozpuszczania azotanu lantanowo-amonowego
w wodzie. Układ (0) – dane derywatograficzne

No. system	R_0	Heating temperature [°C] initial	Heating temperature [°C] final	Heating time [s]	Heating rate [deg·s]
0	4.0000	22.07	250.11	10140	0.0224
I	5.9326	14.75	90.09	1760	0.0715
II	6.7057	13.05	89.96	1900	0.0582
III	7.2855	10.45	90.04	1720	0.0559
IV	7.8652	9.33	89.75	1880	0.0550
V	8.2518	10.55	90.07	1550	0.0580
VI	9.0248	8.06	92.62	1620	0.0616
VII	9.7979	7.23	90.25	1570	0.0577
VIII	10.5709	9.17	90.22	1630	0.0534
IX	11.3440	2.85	90.00	1650	0.0585
X	12.1170	2.46	90.17	1590	0.0614
XI	12.5035	3.50	90.09	1800	0.0554
XII	12.8901	3.57	89.98	1600	0.0617
XIII	13.2766	3.67	90.00	1630	0.0620
XIV	13.6631	4.94	90.02	1620	0.0621
XV	12.8901	3.34	90.18	1730	0.0558
XVI	12.5035	3.04	90.82	1920	0.0566
XVII	7.8652	13.16	90.85	1400	0.0598
XVIII	7.8652	12.63	90.10	1720	0.0574
XIX	7.8652	14.55	91.66	1760	0.0574
XX	7.8652	9.43	90.06	1690	0.0609
XXI	11.7305	6.35	90.06	2060	0.0574

Table 2. Final temperature of polythermal dissolution – T_S (thickened numerals) corresponding
to second highest maximum of dT and temperature corresponding to maxima localized
in its nearest environment obtained for the process of polythermal dissolution
of lanthanum-ammonium nitrate in water. System (0) – derivatographic data
Temperatura końcowa politermicznego rozpuszczania (T_S – liczby pogrubione)
w drugim najwyższym maksimum dT oraz temperatura maksimów z jego najbliższego
otoczenia, uzyskanych w procesie politermicznego rozpuszczania
azotanu lantanowo-amonowego w wodzie. Układ (0) – dane derywatograficzne

No.	Temperature in maximum of dT [°C]							ΔT
system	1.	2.	3.	4.	5.	6.	7.	7-1
0	85.37	86.25	86.98	87.97	88.93	89.78	90.68	5.31
I	75.83	77.22	79.23	81.51	83.59	85.49	87.29	11.46
II	72.24	73.58	74.90	76.78	79.26	81.02	82.40	10.16
III	71.20	72.48	–	75.27	77.18	78.77	80.38	9.18
IV	65.01	66.87	68.60	70.96	73.14	74.93	76.09	11.08
V	65.19	66.59	68.50	70.35	72.03	73.80	75.50	10.31
VI	61.40	62.87	64.42	66.47	68.80	70.60	72.33	10.93
VII	57.04	58.77	60.53	62.18	63.87	65.41	66.61	9.57
VIII	51.62	53.62	55.25	56.77	58.06	60.26	61.79	10.17
IX	43.83	45.58	47.27	48.74	50.53	52.52	54.41	10.58
X	39.86	41.36	43.19	45.00	46.84	48.76	50.50	10.64
XI	38.44	40.64	41.91	43.63	45.19	46.52	47.97	9.53
XII	38.08	39.59	41.26	43.33	44.06	45.96	47.56	9.48
XIII	31.49	33.36	34.56	36.52	38.44	40.36	42.17	10.68
XIV	35.17	36.78	38.45	40.17	42.00	43.66	45.51	10.34
XV	38.28	39.82	41.53	43.15	44.43	46.40	47.58	9.30
XVI	34.35	35.92	37.40	39.12	40.92	42.10	43.56	9.21
XVII	69.41	–	72.03	73.85	75.61	77.34	79.01	9.60
XVIII	68.69	70.07	71.84	73.93	–	76.87	78.61	9.92
XIX	68.99	70.55	72.36	73.85	75.49	76.83	78.35	9.36
XX	64.97	66.30	68.02	69.99	71.67	73.01	74.56	9.59
XXI	40.61	42.26	43.97	45.86	47.60	48.93	50.56	9.95

Table 3. Duration time of individual cycles of polythermal dissolution
of lantanium-ammonium nitrate in water. System (0) – derivatographic data
Czas trwania poszczególnych cykli politermicznego rozpuszczania
azotanu lantanowo-amonowego w wodzie. Układ (0) – dane derywatograficzne

No.	Duration of individual dissolution cycles (sec.)							
system	0^*	1	2	3	4	5	6	1-6
0	2722.1	31.3	22.8	36.2	36.5	28.3	37.0	192.1
I	1416.6	23.7	30.0	26.0	23.5	25.0	31.9	160.1
II	1481.8	28.7	21.7	26.5	37.8	31.8	28.3	174.8
III	1320.6	29.5	–	48.6	29.4	26.5	30.2	164.2
IV	1148.7	38.5	29.4	37.2	36.9	34.7	24.7	201.4
V	1031.6	29.3	34.7	29.0	25.9	28.5	30.4	177.8
VI	919.8	26.6	25.8	31.2	35.6	28.6	29.8	177.6
VII	854.6	32.3	29.6	26.4	27.9	27.1	22.5	165.8
VIII	748.1	41.2	30.6	26.8	22.2	39.5	29.8	190.1
IX	617.5	31.4	28.8	23.8	28.9	33.6	34.2	180.7
X	526.8	26.0	30.1	28.5	28.4	30.9	29.4	173.3
XI	596.7	41.3	22.6	29.8	27.5	24.3	26.6	172.1
XII	480.4	24.4	26.2	32.4	11.6	31.4	27.7	153.7
XIII	407.7	31.1	19.5	31.3	30.0	30.5	29.9	172.3
XIV	470.1	26.7	26.6	26.6	28.9	26.7	31.0	166.5
XV	602.5	28.6	30.8	28.2	22.0	35.2	21.7	166.5
XVI	502.5	30.1	27.0	30.4	30.5	19.8	25.1	162.9
XVII	960.2	–	47.5	27.4	26.5	28.5	30.6	160.5
XVIII	1200.3	28.5	31.4	32.9	–	47.4	32.6	172.8
XIX	1160.5	25.5	28.1	23.8	29.4	26.0	24.1	156.9
XX	1078.5	24.9	27.1	28.8	25.8	22.4	28.6	157.6
XXI	739.0	30.7	30.1	31.9	29.0	22.9	28.7	173.3

column 0^* - time of the first cycle

Table 4. Approximation analysis of initial crystallization temperature (T_0)
and final temperature of dissolution (T_S) of lanthanum-ammonium nitrate as a function of relative
concentration of water(R_0)
Analiza aproksymacyjna początkowej temperatury krystalizacji (T_0) i końcowej temperatury
rozpuszczania (T_S) azotanu lantanowo-amonowego w funkcji stężenia względnego wody (R_0)

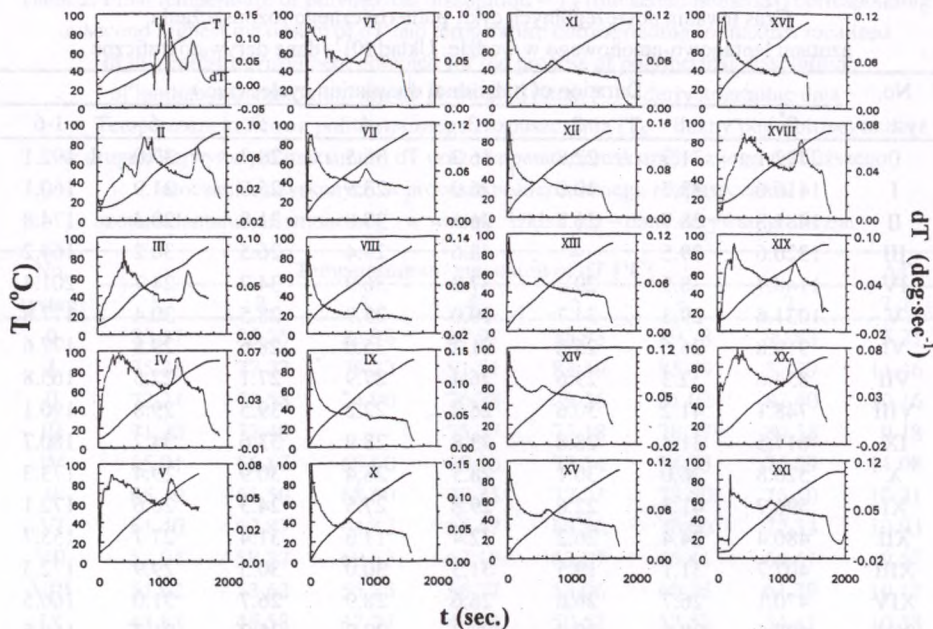| Type	Sum	COD^*	Parameters of line	
function	sqrs		A[0]	A[1]
R_0 vs. T_0	25.1562	0.9920	109.3103	-5.8381
R_0 vs. T_S	29.9764	0.9898	116.4715	-5.7214

COD - coefficient of determination

Fig. 1. Heating curves (T) of the examined systems against the background
of their first derivatives (dT)
Krzywe ogrzewania (T) badanych układów na tle ich pierwszych pochodnych

The above data indicate, that dissolution of lanthanum-ammonium nitrate occurred at higher (by ~7.2°C) temperature than the crystallization process. Qualitative similarity of dissolution and crystallization processes shown in Figure 2 suggests also the similarity of mechanisms of these processes.

For the introductory discussion of mechanism of polythermal dissolution process a part of the heating curve for system XVII ($R_0 = 7.8652$) on the background of its three successive derivatives is plotted (Fig. 3).

Nine vertical lines derived from four zero points, two maxima and three minima of the third derivative (d^3T) determine, as in crystallization [1], two cycles of polythermal dissolution and each cycle includes four phases. Not precise agreement of the second and third zero points of the third derivative with the corresponding maxima of the second derivative seems to be due to the approximate way of mathematical description of the experimental data by means

of the NSpline method [4] and/or thermal inertness of the measurement system as well as fast change of temperature during the dissolution process.
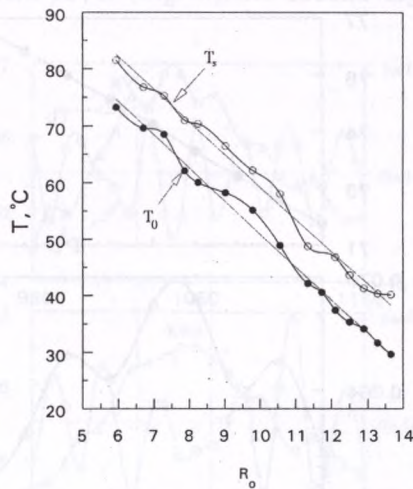

Fig. 2. Linear approximation of final temperature of dissolution (T_S) and initial temperature of crystallization (T_0) [1] as functions of relative concentration of water (R_0)
Aproksymacja liniowa końcowej temperatury rozpuszczania (T_S) i początkowej temperatury krystalizacji (T_0) w funkcji stężenia względnego wody (R_0)

In the deepest minimum of the third derivative (Fig. 3) the system attains the highest heating rate which indicates the termination of crystallic structure destruction of endothermal process. The water molecules evolved during this process form the bonds of stable dipol–stable dipol type [5] increasing additionally the rate of temperature changes. During further heating there takes place weakening of the bonds with participation of the stable dipoles and in 1 (or 1`) phase of dissolution cycle formation of ion–stable dipol type bonds between nitrate, ammonium and lanthanum ions and water molecules occurs. In the phase 2 (or 2`) there is observed a gradual thermal dehydration of the structures formed owing to dissolution of crystallic phase and in the first maximum there appear conditions promoting decomposition of this phase and formation of new structures with the ion-ion type bonds. As in the case of crystallization [1] this process intensifies in phase 3 (or 3`) and ends in phase 4 (or 4`) leading to a dramatic decrease in temperature changes. The water molecules in the first hydration sphere of lanthanum are displaced to the second hydration gradually [6],

form a saturated (molten) solution [7] making it difficult to form highly-
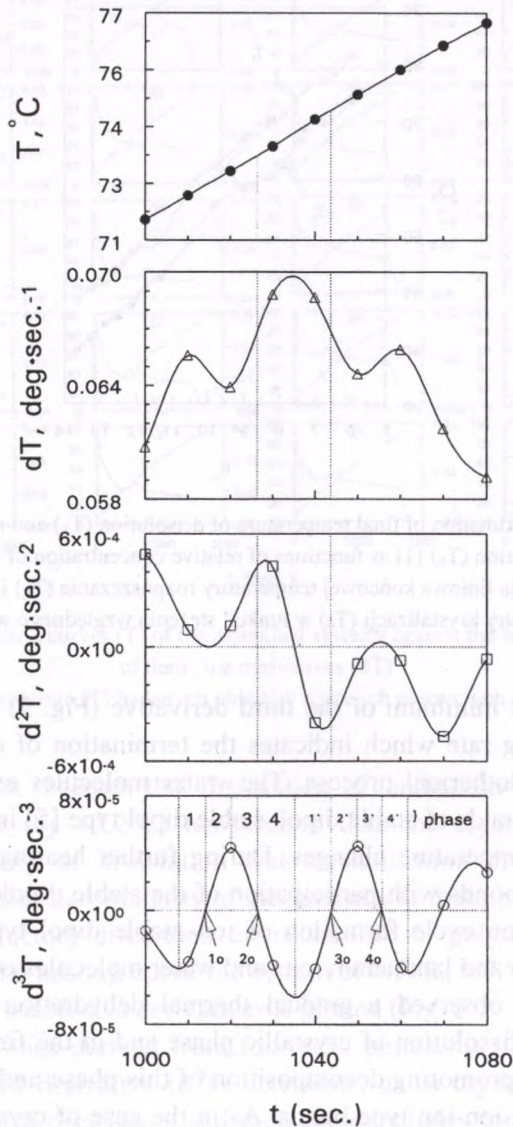-associated (polycondensed) spatial structures.

Fig. 3. Final cycle of dissolution found for system XVII against the background of first (dT),
second (d^2T) and third (d^3T) derivatives of heating curve (T)
Końcowy cykl rozpuszczania w przypadku układu XVII na tle pierwszej,
drugiej i trzeciej pochodnej krzywej ogrzewania (T)

Influence of the heating rate on the shape of kinetic heating curves is shown examplary for XVII–XX systems with the same relative concentration of water ($R_0 = 7.8652$). In system XVII (Fig. 4) the second highest maximum of dT
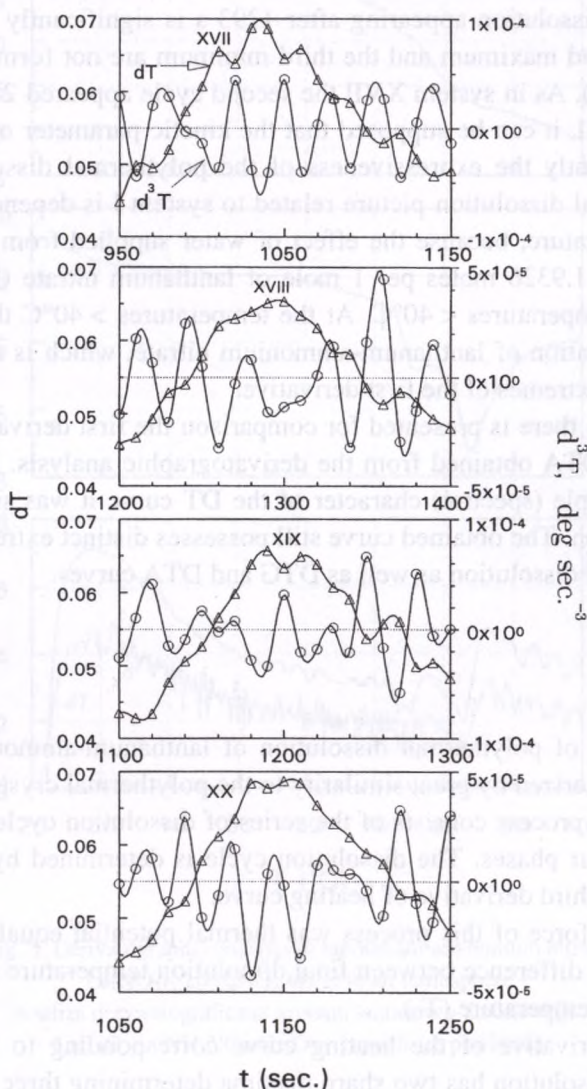
Fig. 4. First (dT) and third (d^3T) derivative of heating curves with six dissolution cycles for the systems characterized by the constant concentration of water ($R_0 = 5.9326$)
Pierwsza (dT) i trzecia (d^3T) pochodna krzywych ogrzewania z sześcioma końcowymi cyklami rozpuszczania w przypadku układów ze stałym stężeniem wody ($R_0 = 7.8652$)

(minimum of d^3T) meaning the termination dissolution process has on the left and right sides two distinct maxima dT (minima of d^3T) which determine two symmetrical cycles of polythermal dissolution. In systems XVIII–XX the symmetry of cycles was disturbed, because, for example, in system XVIII the second cycle of dissolution appearing after 1293 s is significantly broadened, because the second maximum and the third minimum are not formed on the third derivative (d^3T). As in system XVII the second cycle appeared 258s earlier than in system XVIII, it can be supposed that the kinetic parameter of heating influences significantly the expressiveness of the polythermal dissolution picture. The polythermal dissolution picture related to system I is dependent practically only on temperature, because the effect of water supplied from the exterior in the amount of 1.9326 moles per 1 mole of lanthanum nitrate ($R_0 = 5.9326$) is small at the temperatures $< 40°C$. At the temperatures $> 40°C$ there occurs the thermal dehydration of lanthanum-ammonium nitrate, which is reflected in the form of sharp extremes of the first derivative.

In Figure 5 there is presented for comparison the first derivative of TG and T curves and DTA obtained from the derivatographic analysis. Because of the distinctly multiple (spectral) character of the DT curve it was subjected to numerical filtration. The obtained curve still possesses distinct extrema resembling the polythermal dissolution as well as DTG and DTA curves.

4. CONCLUSION

1. The process of polythermal dissolution of lanthanum-ammonium nitrate in water is characterized by great similarity to the polythermal crystallization process. The whole process consists of the series of dissolution cycles and each cycle includes four phases. The dissolution cycle is determined by the succesive minima on the third derivative of heating curve.
2. The driving force of this process was thermal potential equal to ~7.2°C obtained from the difference between final dissolution temperature (T_S) and initial crystallization temperature (T_0).
3. The first derivative of the heating curve corresponding to the process of polythermal dissolution has two sharp maxima determining three regions. In the first region there takes place consumption of heat from the exterior of the system and in the second region thermal dehydration of crystal phase undissolved in water, whereas in the third region heating of the saturated solution is observed.
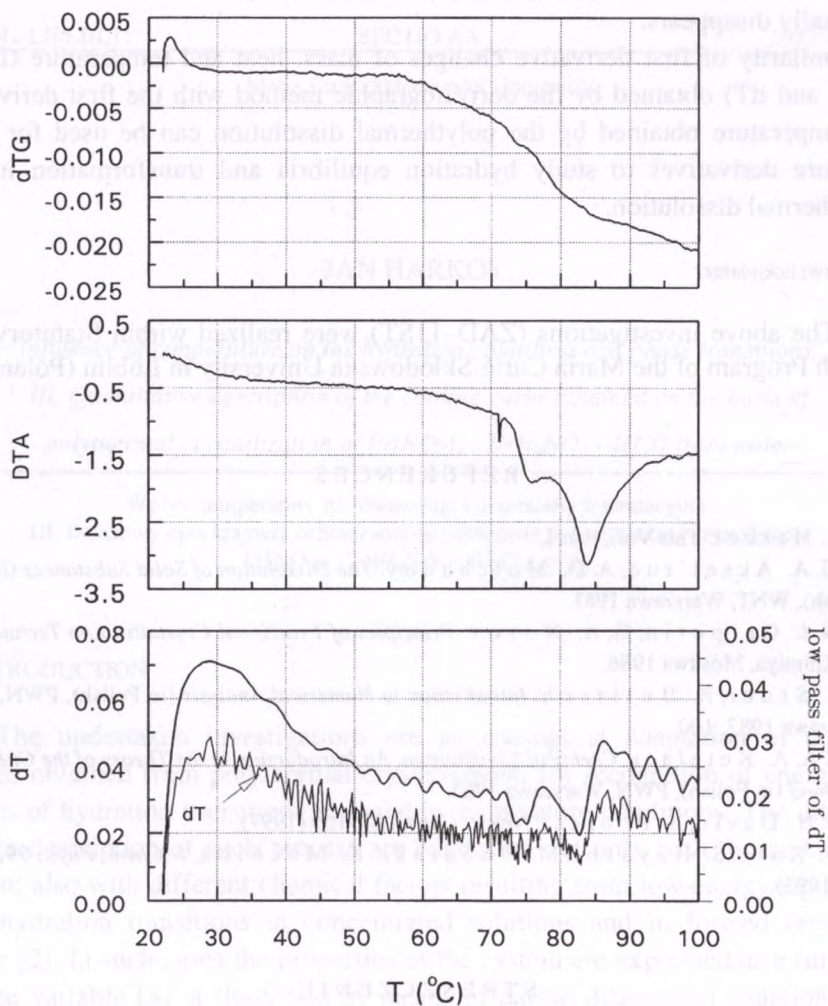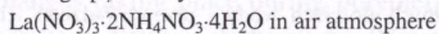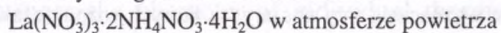
Fig. 5. Derivatographic analysis of lanthanum-ammonium nitrate:
$La(NO_3)_3 \cdot 2NH_4NO_3 \cdot 4H_2O$ in air atmosphere

Analiza derywatograficzna azotanu lantanowo-amonowego:
$La(NO_3)_3 \cdot 2NH_4NO_3 \cdot 4H_2O$ w atmosferze powietrza

4. The picture of polythermal dissolution obtained based on the third derivative of the heating curve is determined mainly by the kinetics of dissolution process, because the parameters of individual cycles of dissolution process are sharply

resolved at high heating rates and with the reduction of these rate this resolution gradually disappears.

5. Similarity of first derivative changes of mass, heat and temperature (DTG, DTA and dT) obtained by the derivatographic method with the first derivative of temperature obtained by the polythermal dissolution can be used for temperature derivatives to study hydration equilibria and transformation in the polythermal dissolution.

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STRESZCZENIE

Zarejestrowano zmiany temperatury w procesie politermicznego rozpuszczania azotanu lantanowo-amonowego w różnych ilościach wody i przeprowadzono ich numeryczne różniczkowanie. Stwierdzono występowanie dwóch mocnych maksimów na pierwszej pochodnej krzywej ogrzewania. Maksima te wyznaczają trzy obszary, w których rozpuszczalność fazy krystalicznej zależy od temeperatury i ilości wody dostarczonej do układu. Ponadto zaobserwowano niewielkie nakładające się na nią maksima, uwidaczniające się coraz wyraźniej przy obniżaniu się stężenia wody w układzie. W oparciu o trzecią pochodną dokonano analizy tych maksimów, przy czym wyznaczono temperaturę i czas ich pojawiania się podczas rozpuszczania. Wskazano na możliwość analizy procesu rozpuszczania na podstawie zależności między temperaturą końcową rozpuszczania (T_S) i stężeniem względnym wody w układzie (R_0).