Journal of Thermal Analysis and Calorimetry, Vol. 88 (2007) 3, 681–686

THE REACTION CONDITIONS INFLUENCE ON SUCROSE ACID HYDROLYSIS STUDIED BY MEANS OF DSC METHOD

Dorina Chambré, Cornelia Idiţoiu[*] *and Maria-Raluca Szabo*

Chemical & Technological Research Center, Food Engineering, Tourism and Environmental Protection Faculty, 'Aurel Vlaicu' University of Arad, E. Dragoi 2, Arad, 310330, Romania

The influence of the reaction conditions upon the sucrose acid hydrolysis to glucose/fructose equimolecular mixture was investigated, in heterogeneous and homogeneous system, by means of DSC method. The recorded DSC signal was used to evaluate the kinetic parameters and the afferent catalytic constant, k_{cat}^{323} values.

In homogeneous conditions the used catalyst was acetic acid while in heterogeneous systems a series of carboxylic resins was used as catalysts. The results show a dependence of the kinetic parameters on homogeneous/heterogeneous catalyst nature and on resins experimental properties (cross-linking degree, granulation, porous nature of polymeric matrix, swelling time).

Keywords: *carboxylic resins catalysts, catalytic kinetic parameters, DSC, homogeneous/heterogeneous acid catalysis, sucrose cationite hydrolysis*

Introduction

One of the actual tendencies of the researches in the alimentary domain is oriented to identify new procedures to obtain natural sweeteners with superior quality usable for the preparation of low calories food.

The industrial methods used these days to obtain food sweeteners, like fructose, are based on enzymatic hydrolysis of starch or sucrose under the action of the invertase (E.C. 3.2.1.26, β-*D*-fructofuranozidase) enzyme [1–4]. These procedures are laborious and costly and this is why it appeared the necessity to use some new methods like heterogeneous acid catalysts. This alternative has imposed itself because of its certain advantages comparing with both enzymatic and homogeneous methods [5–7], like: the rigorous control of the reaction, the reduction of the secondary products content, easier separation of catalyst from the reaction medium, lower cost of catalyst/unit of product, absence of the equipment corrosion, the possibility to pilot the catalytic processes at higher temperatures than in the case of enzyme processing which strongly favors the equilibrium displacement to the reaction products [8].

In this context fits a series of our previous researches referring to the possibility to obtain fructose by heterogenising the acid hydrolysis of sucrose (1) in the presence of some carboxylic cationites from cationic synthetic resins [9–12].

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{catalyst}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6} \qquad (1)$$

Continuing these studies, an analysis of the reaction conditions over the reaction kinetics has been done in this paper. The heterogeneous catalysts used in the experiments were low acid cationic resins with carboxylic functional groups of Purolite type. We have been chosen these resins because of their versatile properties and due to their high purity degree, they became potential catalysts for different aqueous processes from the food industry [13].

In order to compare the kinetics of this reaction conducted under heterogeneous and homogeneous conditions, in some of the experiments the acetic acid was used as catalyst.

The practical scope of this work is therefore to examine how the homogeneous/heterogeneous nature of the studied catalysts, respectively the characteristics of the heterogeneous carboxylic catalysts (cross linking degree, exchange capacity, porous/gel nature of the polymeric matrix, granulation and swollen time) influence the values of the kinetic parameters and of catalytic constants, k_{cat}, afferent to the acid hydrolysis of the sucrose, investigated by DSC measurements.

This analysis is justified by the fact that the studies presented in the literature mention that the experimental parameters (the working conditions and the catalysts characteristics) are influencing the values of the apparent kinetic constants in aqueous [14, 15] or non-aqueous medium [16] catalyzed by the ion-exchange resins, and overall kinetic of these reactions, depends on the different limitative steps [17, 18].

---

[*] Author for correspondence: corneliaiditoiu@yahoo.com

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

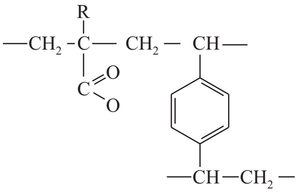
Experimental

Materials

The main characteristics of the synthetic cationites, in acid (H^+) form, used in the experiments are presented in Table 1.

For the reactions in homogeneous catalytic medium, the acetic acid, from Merck was used as catalyst. In all experiments, sucrose (from Merck) was used as aqueous solution with C_0=1 M. The volume of this solution, added over cationite, was V_{sol}=100 μL.

The investigations were made on a series of synthetic carboxylic cationites of Purolite type, in macroporous or gel form, with different granulations, exchange capacities (C_0) and cross-linking degree (DVB%). The investigated resins had a polymeric matrix based on acrylic acid cross-linked with divinyl-benzene (Scheme 1). The cationites, used in these experiments, were made by Purolite International Ltd.Co. from England.



Scheme 1 where: R: –H

Methods

In order to follow the sucrose hydrolysis in the presence of carboxylic cationites and acetic acid respectively, the DSC technique was used.

The experiments were done using a microDSC III calorimeter (SETARAM Group, France), fitted with two identical 'cells' (the reference cell R and the measurement cell S) made from steel cylinders of 1 cm^3 volume.

The temperature program (used for all experiments) was: (1) cooling from 25 to 10°C with a rate of 2.5 K min^{-1} (maximum allowed); (2) system thermostating to 10°C for 10 min; (3) heating from 10 to 95°C with a heating rate of 0.15 K min^{-1} in order to obtain the afferent DSC signal for the reaction; (4) cooling from 95 to 10°C with a rate of 2.5 K min^{-1}; (5) maintaining the system at 10°C for 600 s; (6) heating from 10 to 95°C with a heating rate of 0.15 K min^{-1} (for the baseline); (7) cooling from 95 to 25°C with 2.5 K min^{-1}.

The heterogeneous experiments were done using different cationite amounts, which were swollen with deionizated water for 10, 24, 36 or 48 h at 20°C. The swelling process was done directly in the S cell, where it was introduced measured amounts of dry resin and a pre-established water volume to avoid excess. Both, R and S cells, with swollen cationite were submitted to (1) and (2) sequences from the temperature program. After 10 min of isothermal conditions at 10°C, in the S cell were introduced, with a micro-syringe, 100 μL sucrose solution 1 M with temperature of 10°C under shaking condition in order to obtain an uniform distribution of reactant in the swollen cationite mass. After injecting sucrose in the S cell, the system was at once submitted to the (3)–(7) sequences with the aim to obtain the calorimetric data starting with the beginning of the reaction.

In a similar way it has been proceeded in the presence of the acetic acid as reaction catalyst, at about the same concentration of the carboxylic catalytic groups as in heterogeneous catalyst experiments.

Results and discussions

The shape of the DSC calorimetric signal for one experiment of sucrose acid hydrolysis catalyzed by the carboxylic cationite Purolite C 106 EP resin with 35–50 mesh granulation is shown in Fig. 1.

Similar DSC signals were obtained for all cationite and acetic acid experiments.

Table 1 Main characteristics of the synthetic cationites in acid (H^+) form used in the experiments [13]

No.	Cationite	Polymeric matrix type	Cross-linking degree DVB%	Exchange capacity, C_0/mEq g^{-1}	Granulation (mesh)
1.	Purolite C 104	macroporous	10	9.42	35–50
2.	Purolite C 105	gel	7.2	9.38	14–20 20–30 30–35 50–60 60–70
3.	Purolite C 106	macroporous	12	9.31	35–50
4.	Purolite C 106 EP Special for food industry	gel	12	9.29	35–50
5.	Purolite C 107 E Special for food industry	macroporous	9	9.69	35–50

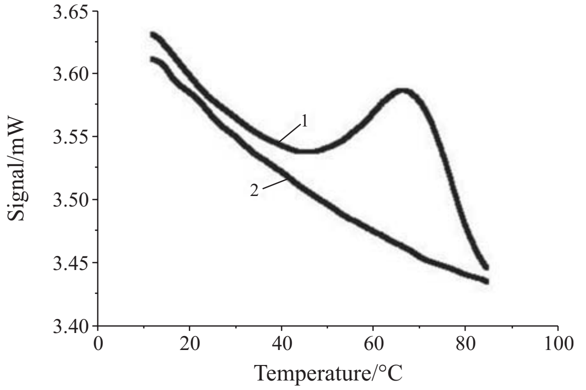


Fig. 1 DSC signal for the sucrose hydrolysis reaction catalysed by Purolite C106 EP cationite with 35–50 mesh and C_1=2.09 mEq$_{COOH}$ g^{-1} mixture 1 – calorimetric signal, 2 – base-line

After separation of the calorimetric signal from the base-line, it has been processed and analyzed as to evaluate the reactant conversion degree, α (Eq. (2)), at different moments, *t*, from the reaction start [10, 11].

$$\alpha = \frac{a}{A^*} \tag{2}$$

where: α – the reaction progress degree at a certain moment, *t*, from the reaction starting; *a* – the partial area at the *T* temperature; *A** – the total area of the DSC curve.

The dependence of the reactant conversion, α, upon temperature for different concentrations of the catalytic species is presented Fig. 2.

From the obtained experimental data, the values of the apparent kinetic parameters were calculated with the relation (3) where, for the conversion function, *f*(α), it was used the Eq. (4) form [19], because the sucrose acid hydrolysis has first apparent reaction order [19, 20].

$$\ln\beta\frac{d\alpha}{dT} - \ln f(\alpha) = \ln A - \frac{E}{RT} \tag{3}$$

$$f(\alpha) = (1-\alpha)^1 \tag{4}$$

After the Eq. (4) plotting it was obtained a series of straight lines from which the activation energy, *E* and the pre-exponential factor, *A*, were evaluated.

Using the known Arrhenius Eq. (5), the values of the apparent kinetic constants, k_{ap}^{323}, were calculated for *T*=323 K.

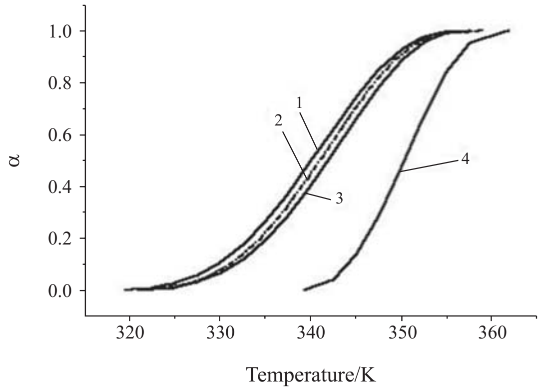


Fig. 2 The dependence of the reaction progress degree, α, on the temperature, for different Purolite C106EP (35–50 mesh) catalyst concentrations: 1 – C_{het}=2.09; 2 – C_{het}=1.89; 3 – C_{het}=1.64 (mEq$_{COOH}$ g^{-1} mixture); 4 – C_{hom}=2.08 (mEq acetic acid g^{-1} mixture)

$$k_{ap} = Ae^{-\frac{E}{RT}} \tag{5}$$

where: *A* – pre-exponential factor (s^{-1}), *E* – activation energy (kJ mol^{-1}), *T* – temperature (K), *R* – the general constant of gases (kJ mol^{-1} K^{-1}).

The values of the catalytic kinetic constants, k_{cat}^{323}, were evaluated, in all cases, based on Eq. (6) [10, 19].

$$\ln k_{ap}^{323} = \ln k_{cat}^{323} + m \ln C_{COOH} \tag{6}$$

where: *m* – the catalytic reaction order, C_{COOH} – the concentration of the catalytic moieties in the reactant system (m Eq g^{-1} mixture).

The influence of the catalyst nature

The influence of the homogeneous/heterogeneous nature of the catalyst over the apparent kinetic parameters (*A*, *E*, k_{ap}^{323}), for the acid sucrose hydrolysis, is shown in Table 2 when Purolite C106 EP and acetic acid were used as catalysts, at about the same concentration of the catalytic species in the reaction system namely 2 mEq g^{-1} mixture.

From the above data it can be noticed that, for equal catalyst concentrations, the k_{ap}^{323} values are about 18 times higher in heterogeneous system than in homogeneous one. This may suggest that, in the case of the sucrose acid hydrolysis, the cationite as heterogeneous catalyst has a higher catalytic activity than of the homo-

Table 2 The apparent kinetic parameters *A*, *E* and k_{ap}^{323} for the sucrose acid hydrolysis

No.	Catalyst	C_{cat}/ mEq$_{COOH}$g^{-1} mixture)	*A*/ s^{-1}	*E*/ kJ mol^{-1}	k_{ap}^{323}/ s^{-1}	*r**
1.	Purolite C 106 EP 35–50 mesh	2.10	$3.66\cdot10^{15}\pm0.52$	122.86±0.17	$4.90\cdot10^{-5}$	–0.9994
2.	Acetic acid	2.08	$5.70\cdot10^{25}\pm0.12$	193.60±0.44	$2.69\cdot10^{-6}$	–0.9992

* – correlation factor

Table 3 The dependency of the catalytic kinetic constant, k_{cat}^{323}, and of the reaction catalytic orders, m_{cat}, on the catalyst heterogeneous/homogeneous nature

No.	Catalyst	k_{cat}^{323}/s^{-1}	m_{cat}	r*
1.	Purolite C106EP	$1.07\cdot10^{-5}$	~2.0	0.9990
2.	Acid acetic	$9.50\cdot10^{-7}$	~ 1.4	0.9990

* – correlation factor

geneous acetic acid. Elsewhere [21] it has been mentioned a similar behavior for the cumen hydroperoxide acid decomposition on sulphonic resins as heterogeneous catalyst and para-tolue-sulphonic acid as homogeneous catalyst in anhydrous medium.

In Table 3 is presented the dependency of the catalytic kinetic constant values, k_{cat}^{323}, and of the reaction orders, m_{cat}, on the nature of the used catalyst.

As it can be noticed from Table 3, for the sucrose acid hydrolysis in aqueous solution, the value of the kinetic catalytic constant, k_{cat}^{323}, in heterogeneous system is about 100 respectively 29 times higher than in the case of homogeneous catalysis, when acetic and chlorhydric [20] acids are used as catalysts.

Also the value of the catalytic order, m_{cat}, is higher in the case of the heterogeneous than in the homogeneous catalyst.

A possible explanation for those values is the resin structure that it makes possible to realize higher local ‘concentration’ of the catalytic groups than in homogeneous medium. Under those conditions the –COOH groups from the cationite may present a concerted action over the substrate, impossible to be achieved, at the usual catalyst concentrations, in the homogeneous systems [17, 21]. It was found that DSC is an appropriate method to study the bound formation and breaking on heterogeneous catalyst surfaces [22].

The influence of the cross-linking degree and of the gravimetric exchange capacity

The influence of the cross-linking degree (%DVB) of the carboxylic cationites on the overall reaction kinetic is presented in Table 4.

From Table 4 data it can be inferred that as cross-linking degree increases from 9 to 12%DVB, the values of the catalytic kinetic constant, k_{cat}^{323}, are decreasing with about two-size orders. Thus the use as catalyst of the macroporous Purolite C107 E (special for the food industry) that has the smallest cross-linking degree conducted to the getting of the highest value for the catalytic kinetic constant.

This behavior can be explained by the existence of a diffusional hindrance due to the polymeric matrix reticulant. Under those conditions, the access of the reactants to the –COOH catalytic groups is limited and therefore overall kinetic of the sucrose acid hydrolysis in the presence of the carboxylic cationites is diminished.

On the other side, it should be considered that, with the increase of the cross-linking degree of the resins, the values of the exchange capacities are decreasing, or the global rate for the heterogeneous sucrose hydrolysis reaction depends on the number of the –COOH groups available in the reaction system.

Therefore we can conclude that the studied catalytic process is mainly controlled by the chemical act that takes place on the –COOH active centers of the resin matrix on which the diffusion hindrance is overlapped.

The influence of the porous /gel nature of the polymeric matrix

The dependence of the catalytic kinetic constants, k_{cat}^{323}, of the sucrose acid hydrolysis upon the porous/gel nature of the polymeric matrix of the carboxylic cationites, used as catalysts, is shown in Table 5.

From Table 5 results that, for the same cross-linking degree, macroporous resin catalyst has a higher activity of about 40 times than the gel resin, even if it has been all right swelled.

These values suggest that in gel resins case, the internal diffusion of the reactant molecules is a limitative step upon the global chemical kinetic.

It can also be noticed the large differences between k_{cat}^{323} values of Purolite C106 resin swollen for 36 h (Table 5) and the one swollen for 24 h (Table 4).

The granulation influence

The granulation of heterogeneous catalysts is one of diffusion parameters, therefore it is expected to influ-

Tabel 4 The influence of the cross–linking degree of the macroporous carboxylic catalysts on the values of the catalytic kinetic constants, k_{cat}^{323}, (35–50 mesh, swollen time 24 h)

No.	Cationite	Cross–linking degree/ DVB%	Exchange capacity, C_0/ mEq g^{-1}	k_{cat}^{323} /s^{-1}	r*
1.	Purolite C 107 E	9	9.69	$5.42\cdot10^{-3}$	0.9992
2.	Purolite C 104	10	9.42	$3.51\cdot10^{-4}$	0.9990
3.	Purolite C 106	12	9.31	$6.98\cdot10^{-5}$	0.9994

* – correlation factor

Table 5 The influence of the porous/gel nature of the polymeric matrix of the carboxylic catalysts on the values of the catalytic kinetic constants, k_{cat}^{323}, of the sucrose acid hydrolysis (35–50 mesh, swollen time: 36 h)

No.	Catalyst	Matrix porous/ gel nature	Cross-linking degree/ DVB%	k_{cat}^{323}/s^{-1}	r*
1.	Purolite C 106 EP	gel	12	$1.072\cdot10^{-5}$	0.9990
2.	Purolite C 106	macroporous	12	$3.988\cdot10^{-4}$	0.9992

* – correlation factor

Table 6 The influence of the carboxylic catalysts granulation over the values of the catalytic kinetic constants, k_{cat}^{323} (swelling time: 36 h)

No.	Cationite	Cross-linking degree/DVB%	Exchange capacity C_0/mEq g^{-1}	Granulation/ mesh	k_{cat}^{323}/s^{-1}	r*
1.	Purolite C 105	7.2	9.38	14–20	$3.16\cdot10^{-5}$	0.9987
2.				20–30	$4.88\cdot10^{-5}$	0.9993
3.				30–35	$7.48\cdot10^{-5}$	0.9988
4.				50–60	$3.12\cdot10^{-4}$	0.9993
5.				60–70	$5.51\cdot10^{-4}$	0.9994

* – correlation factor

ence the global kinetics of catalytic reaction also when carboxylic cationite are used as acid catalysts. The dependence of overall kinetics for sucrose hydrolysis upon the resin granulation is shown in Table 6.

From Table 6 it can be noticed that with the decrease of the catalyst granulation from 14–20 mesh to 60–70 mesh, the value of the catalytic kinetic constant, k_{cat}^{323}, is increasing about 18 time. An explanation for this behavior is based on the fact that, the smaller granules are putting to the reactant disposition a higher contact surface and so, a higher number of superficially active –COOH centers, easy to be accessed by the reactants, on which the reaction can take place.

The literature data emphasize that gel resins, in dry state, are catalytical inactive [17,18]. Under these conditions, the use of the gel type cationites, as catalysts, requires the presence of a swelling medium that creates the 'micropores filled with liquid' structure, which ensures the access of the reactants to the catalytic centers from the internal micropores [17].

For practice, it is recommended that both gel or macroporous cationite type to be submitted for a swelling process and for different time periods, before their use in ionic or catalytic processes [9, 17].

The influence of the swelling time

The influence of the swelling time of the catalyst on the catalytic constant values, k_{cat}^{323}, of the sucrose acid hydrolysis is shown in Table 7.

From Table 7 data it can be seen that for both cationite types, the increase of the swelling time (from 10 to 48 h) is followed by an increase of the catalytic kinetic constant, k_{cat}^{323}, values. It can be also noticed that, for the macroporous Purolite C 107 E resin the minimum swelling time is 24–36 h, while for the gel Purolite C 106 EP cationite it is larger, i.e. about 48 h.

Table 7 The influence of the swelling time of the carboxylic catalyst granules over the catalytic constant values, k_{cat}^{323} (granulation: 35–50 mesh)

No.	Cationite	Swelling time at 20°C/h	k_{cat}^{323}/s^{-1}	r*
1.	Purolite C107E macroporous	10	$2.35\cdot10^{-3}$	0.9994
2.		24	$5.42\cdot10^{-3}$	0.9990
3.		36	$5.44\cdot10^{-3}$	0.9992
4.		48	$5.44\cdot10^{-3}$	0.9995
5.	Purolite C 106 EP gel type	10	$5.11\cdot10^{-6}$	0.9990
6.		24	$1.06\cdot10^{-6}$	0.9991
7.		36	$1.07\cdot10^{-5}$	0.9990
8.		48	$1.07\cdot10^{-5}$	0.9990

* – correlation factor

Creating the micropores structure filled with liquid produces the removal of the polymeric chains and it favors the diffusion of the reactants inside the catalysts granules and it eases the reactant access to the internal catalytic active groups.

The minimum swelling time must be established individually for each cationite type and it is influenced both by the porous nature of the polymeric matrix and by the cross-linking degree.

A well-done swelling process of the resins, allows to obtain the kinetic catalytic constants, k_{cat}^{323}, which are not influenced by the diffusion processes.

From Table 7 data, results that the real value of the catalytic constant when chemical process is a limitative step is about $5.44\cdot 10^{-3}$ (s^{-1}) and it is achieved in our experiments only for the macroporous Purolite C107 E resin, with the lowest cross-linking degree.

In all other cases, the diffusion process is the limitative step and it diminishes, more or less, the real k_{cat}^{323} values afferent to the chemical process.

Conclusions

The DSC study of the sucrose acid catalyzed hydrolysis proved that there is a large influence of the catalyst homogeneous/heterogeneous nature upon chemical process, which also depends on diffusion characteristics of resin catalysts like: cross-linking degree, exchange capacity, granulation, porous/gel nature of the polymeric matrix, swelling time.

The values of the catalytic kinetic constant, k_{cat}^{323}, and of the catalytic reaction order, m_{cat}, obtained in the heterogeneous system are well higher than in the homogeneous one.

The reaction rate and implicit the value of the apparent kinetic constant, k_{ap}^{323}, depends on the number of the active catalytic groups, easy accessible to the reactants.

The global catalytic process is mainly controlled by the chemical reaction that takes place, on the internal and external active centers, over which overlaps the reactants diffusion inside the pores of the catalyst granules which is also limitated by the cross-linking degree.

The use of the carboxylic cationite resins, as catalysts, requires a certain swelling time (24–36 h the macroporous cationites and 36–48 h the gel type cationites) for the creation of the micropores structure filled with liquid that favors the reactant access to the internal catalytic active groups.

The minimum swelling time has to be established individually for each type of cationite because it is influenced both by the porous/gel nature of the polymeric matrix and by the cross-linking degree (%DVB).

A well-done swelling combined with an adequate porosity of the resins allows to obtain k_{cat}^{323} values which are non-influenced by the diffusion process. In our experiment conditions this value is $k_{\mathrm{cat}}^{323}=5.44\cdot 10^{-3}$ (s^{-1}) and it was achieved only for the macroporous Purolite C107E resin with 9% DVB.

Acknowledgements

Thanks are due to professor Attilio Cesàro from University of Trieste, B.B.C.M. Department, for permission to use DSC facilities and for helpful suggestions to D.C.

References

1 H. D. Belitz, W. Grosch and P. Schieberle, ‘Food Chemistry’, 3rd revised Edition, Springer, 2004, p. 875.
2 S. Kiran, A. Sikander, E. Amna and H. Ikram-ul, OnLine J. Biol. Sci., 3 (2003) 1991.
3 U. C. Filho, C. E. Hori and E. J. Ribeiro, Braz. J. Chem. Eng., 16 (1999) 1.
4 K. Kouassi and Y. H. Roos, J. Agric. Food Chem., 48 (2000) 2461.
5 W. Neier, ‘Ion exchangers as catalysts’, Ed. Walter der Gruyter, Germany,1991, p. 1060.
6 T. J. McGovern and J. S. Dranoff, AIChE J., 16 (2004) 536.
7 L. M. Cunha and F. A. R. Oliveira, J. Food Eng., 46 (2000) 53.
8 G. Siegers and F. Martinola, Int. Sugar, 87 (1985) 23.
9 D. Chambre, C. Idiţoiu, E. Segal and R. Szabo, Annals of West University of Timisoara, Series Chemistry, 12 (2003) 1591.
10 D. Chambre, C. Idiţoiu, P. Budrugeac and E. Segal, Rev. Chim. (Bucureşti), 56 (2005) 502.
11 D. Chambre, C. Idiţoiu, E. Segal and A. Cesaro, J. Therm. Anal. Cal., 82 (2005) 802.
12 C. Idiţoiu, D. Chambre, C. Danciulescu and R. Szabo, Sci. Tech. Bull., ‘Aurel Vlaicu’ University of Arad, Series Chemistry, Food Sci. Eng., 6 (2001) 22.
13 Purolite.co., ‘Ion Exchange Resines’, Tehnical Book, U.K. 1998.
14 K. Suchocka-Galas, Eur. Polym. J., 5 (1994) 609.
15 C. Ung-Kyung, Waste Management, 18 (1998) 183.
16 C. Idiţoiu, M. Bura and G. Alexandrescu, Rev. Chim., 35 (1986) 109.
17 F. Helfferich, ‘Ion Exchange’, Mc.Graw-Hill, N.Y. 1962, p. 206.
18 M. Marhol, ‘Ion Exchangers in Analytical Chemistry’, Elsevier Sci. Publ. Comp., N.Y. 1982, p. 102.
19 E. Segal and D. Fătu, ‘Introducere in Cinetica Neizoterma’, Ed. Acad. R. S. R., Bucureşti 1983, p. 142.
20 A. Cesaro, F. Delben and S. Paoletti, Gaz. Chim. Ital., 113 (1982) 387.
21 C. Idiţoiu, E. Segal and B. C. Gates, J. Catal., 54 (1978) 442.
22 J. Bujdák and B. M. Rode, J. Therm. Anal. Cal., 73 (2003) 797.

DOI: 10.1007/s10973-006-8043-y