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Simulations for evaluation of kinetic methods in differential scanning calorimetry. Part 1. Application to single-peak methods: Freeman–Carroll, Ellerstein, Achar–Brindley–Sharp and multiple linear regression methods

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Abstract

In order to simplify the choice between different kinetic methods used in differential scanning calorimetry, an interesting way for testing kinetic treatments is proposed, using simulated thermoanalytical curves computed from given kinetic parameters. Applied to the study of a polymerization, we tested the Freeman–Carroll, Ellerstein, multiple linear regression (reaction-order model) and Achar–Brindley–Sharp methods. The test of the validity of the methods is performed using the LSM parameter that represents the fit between the mathematical treatment used in the kinetic model and known data. The study reveals the importance of the number of points used, i.e. the resolution, in the thermoanalyitcal curve recording, especially for the Freeman–Carroll and Ellerstein methods, there being an increase in the relative error on all the kinetic parameters when the number of points is decreased. Maximum relative errors are reported for the pre-exponential factor calculations. Evaluation of the enthalpy error on the determination of the kinetic parameters has been performed. Simulations obtained with various enthalpies indicate the necessity in such cases of computing a relative dimensionless LSM parameter (relative to the amplitude of the phenomena) in order to compare different thermal effects.

Keywords: Differential scanning calorimetry; Kinetics; Polymerization; Simulations; Thermal analysis;

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1. Introduction

Experimental thermoanalytical curves may be the result of the superposition of several phenomena. For example, in a previous work we attempted to estimate the effect of the heat of the polymerization itself on the temperature estimated and then on the apparent kinetic parameter values [1]. Furthermore, it is known that "difference-differential" methods are very sensitive to the quality of the experimental data [2]. Thus, in this paper, we will try to ascertain whether the mathematical treatment introduces additional uncertainty from the computation itself or from the approximations used [3]. For this, a comparative kinetic study was performed from simulated thermoanalytical curves; the generation of the simulated data is presented in section 2, below. The validity of the single-peak methods is discussed in section 3, where the multiple linear regression [4, 5], Achar–Brindley–Sharp [6], Freeman–Carroll and Ellerstein [7, 8] methods are checked. Care must be taken in interpreting the meaning of the different errors in the calculation. The true values of the parameters of the thermoanalytical curves are not known, even in the case of simulations, because uncertainty in calculation always exists when artificial data are synthesized; therefore, we will call them reference parameters. Nevertheless, absolute relative errors have been computed by comparing the value obtained to that of a reference (the values mentioned are always absolute relative errors).

In earlier papers, we have reported interest in the use of a parameter (called LSM) to evaluate the quality of the fit between the mathematical treatment used in kinetic models and experimental data (mean square error) [1, 9], during a differential scanning calorimetry analysis; this has been defined as

$$\mathrm{LSM} = \frac{1}{N}\sum_i (Y_{i,\mathrm{exp}} - Y_{i,\mathrm{calc}})^2$$

where N is the number of experimental values and Y represents the heat flow measured (exp) or calculated (calc) from the kinetic parameters.

The LSM allows evaluation of the accuracy between computed data (generated from kinetic parameters) and experimental data, i.e. the thermoanalytical curve obtained, which represents the dynamic response of the apparatus used (if not the real phenomenon). The LSM parameter expresses here the fit between computed data and simulated thermoanalytical curves and gives the only available information when the parameters of the transformation are not known.

2. Numerical simulations

These simulations consisted of the computation of the temperature (T_i), of the power (P_i) and the conversion range (α_i) of a known transformation, i.e. a thermoanalytical curve, from known kinetic parameters, sampling rate, heating rate, temperature at the beginning of the phenomenon (T_0) and enthalpy (ΔH). Taking the general kinetic equation for the reaction rate

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_i = k_i f(\alpha_i) \tag{1}$$

with $\alpha_i = H_i/\Delta H$ and $k_i = k_0 \mathrm{e}^{-E_a/RT_i}$, where E_a, k_0 and R represent respectively the activation energy, the pre-exponential factor and the gas constant (8.31 J mol^{-1} K^{-1}), k_i the constant rate and H_i the partial area computed at time i

$$\left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)_i = \Delta H k_i f(\alpha_i) \tag{2}$$

where $(\mathrm{d}H/\mathrm{d}t)_i$ represents the heat flux (P_i) of a DSC scan at time i. Each flux (P_i) corresponding to each temperature (T_i) programmed during a heating cycle may be computed from the knowledge of E_a, $\ln k_0$, $f(\alpha_i)$, ΔH and T_0.

As is sometimes done by calorimeter manufacturers, the term "sampling rate" is related to the interval, expressed in seconds, between the acquisition of two points; but in data processing, the sampling rate has the dimension of the inverse of time and represents the number of recorded points per second. This explains why in this study the number of recorded points increases when the "sampling rate" decreases.

In this paper, the parameters used in the simulations were taken as: reaction enthalpy, $\Delta H = -77$ J; scanning (or here heating) rate, $V = 5°\,\mathrm{min}^{-1}$ and various "sampling rate" values from 1 to 80 s; kinetic order, $n = 2$; pre-exponential factor, $k_0 = 1.78482 \times 10^8\,\mathrm{s}^{-1}$ ($\ln k_0 = 19$); activation energy, $E_a = 77$ kJ mol^{-1}. These values were previously obtained from an experimental polymerization [1]. As we have shown [10], the polymerization experimentally studied can be fitted in the 10–80% kinetic interval with the kinetic homogeneous law $f(\alpha_i) = (1 - \alpha_i)^n$, so that each α_i can be computed as described by Vergnaud and coworkers [11, 12]. From the general kinetic equation we can obtain

$$\frac{\mathrm{d}\alpha_i}{f(\alpha_i)} = k_i \mathrm{d}t \tag{3}$$

$$\int_0^{\alpha_i} \frac{\mathrm{d}\alpha_i}{(1-\alpha_i)^n} = \int_0^{t_i} k_i \mathrm{d}t \equiv S_i \tag{4}$$

$$\alpha_i = 1 - [1 + (n-1)S_i]^{1/1-n} \tag{5}$$

The computation was stopped for an α_i value near to one (> 0.999999). Taking different sampling rate values in our model, it was possible to perform the same computations using constant kinetic and thermodynamic parameters.

3. Results of numerical simulations

As can be seen from Fig. 1 where the relative error on the enthalpy value is given as a function of the sampling rate, there is an accurate determination of the enthalpy for all the sampling rates studied. As an example of the suitability of the proposed simulation,

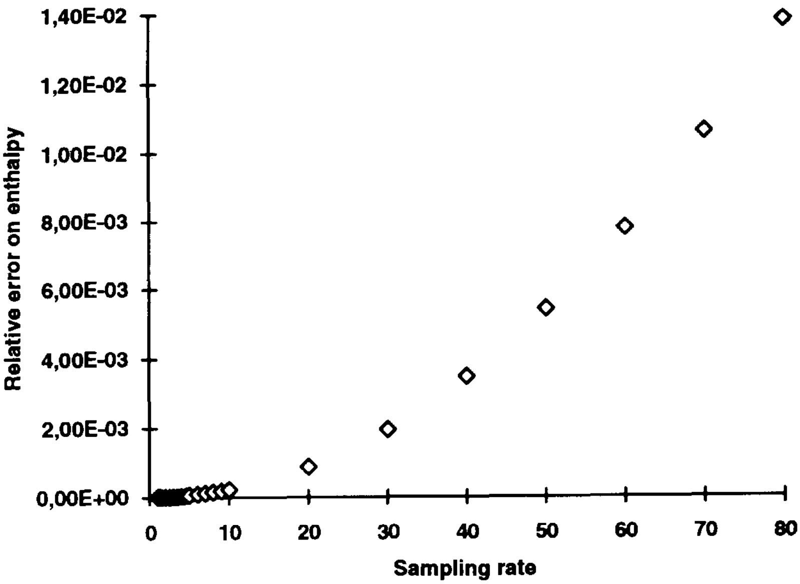

Fig. 1. Relative errors on the enthalpy vs. the sampling rate.

we can examine the enthalpy value found for a sampling rate of 7, i.e. 992 recorded points; the enthalpy is $\Delta H = 76.99121$ J (reference value of 77.00000 J), that is to say a relative error of 1.14×10^{-4}. The integration method used (trapezoidal method as in the commercial software of the DSC) induces a dependence of the relative error on the enthalpy value vs. the sampling rate (Fig. 1). There is a very sharp decrease in the relative error on the enthalpy value when the sampling rate decreases, i.e. the number of recorded points increases. For example, the enthalpy is equal to 75.94122 and 76.99926 J for sampling rates of 80 (88 recorded points) and 1 (6932 recorded points); this means relative errors of 1.38×10^{-2} and 9.66×10^{-6} respectively for the extreme points taken in these simulations.

Evaluation of the kinetic parameters was performed on the artificially created data using the Achar–Brindley–Sharp method, the multiple linear regression method based here on the reaction order model [10], and the methods of Ellerstein and Freeman–Carroll, generally established for reactions that fulfil the kinetic homogeneous law [3]. The logarithmic form of the reaction rate equation may be expressed, for the kinetic homogeneous law, as

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_i = \ln k_0 - \frac{E_a}{RT_i} + n\ln(1-\alpha_i) \tag{6}$$

For the multiple linear regression method, this equation is solved using a multiple regression analysis [4, 5].

Most of the kinetic studies carried out in thermal analysis (differential thermal analysis or thermogravimetry) have been made using 5–22 data points for calculations, or a number of points not specified [13–16]. The aim of this paper is to evaluate, for a differential scanning analysis, the influence of the number of points on the kinetic parameters, according to the kinetic method used. For a given experiment, the number of recorded points will depend on the duration of the transformation studied, on the scanning rate and on the sampling rate chosen. The kinetic data points are the number of points in the kinetic interval, which does not coincide with the totality of the integrated curve (usually 10–90 or 20–80% of the thermoanalytical curve). This evaluation is of great interest, especially in DSC where the calculation of both enthalpy and conversion range depends on the number of points. For this, the parameters were obtained in a first step, using only 10 kinetic data points (88 recorded points). In this case (Table 1) agreement between the evaluated parameters of activation energy and pre-exponential factor from the Achar–Brindley–Sharp, multiple linear regression and Freeman–Carroll methods and the reference parameters is rather poor (for simulated data), while for the reaction order and especially for the pre-exponential factor, significant deviations are found for the Ellerstein method.

In order to evaluate the accuracy of the four methods, it was convenient to determine the influence of the variation of the kinetic data points on the different kinetic parameter values, as it can be obtained experimentally in the case of various recordings. Comparing the results obtained with the highest and lowest number of points used in these simulations (Tables 1 and 2) shows that as the number of kinetic data points increases, the calculated activation energy and pre-exponential factor increase, while the kinetic order decreases (except for Ellerstein's method), the obtained values for the kinetic parameters being nearest in all cases to the reference values for each method. We found a very good accuracy for each method, while LSM values (Table 3) show the superiority of the multiple linear regression method followed by that of Achar–Brindley–Sharp.

Further calculations using different numbers of kinetic data points were performed, and the results are given in Figs. 2–8. The relative error on all the kinetic parameters is decreased when the number of points used is increased, with a factor decrease of about 100 from 10 to 780 data kinetic points, whatever the method used. Table 1 and Figs. 2

Table 1
Evaluation of the kinetic parameters obtained using the Achar–Brindley–Sharp (ABS), multiple linear regression (MLR), Freeman–Carroll (FC) and Ellerstein (EL) methods in the 10–90% interval using 10 kinetic data points

	$n^{a,b}$	er $(n)^c$	$k_0 \times 10^{-08\,a,b}$	er$(k_0)^c$	$E_a^{a,b}$	er $(E_a)^c$
ABS	2.01	–	1.07715	3.96×10^{-01}	74.03910	3.85×10^{-02}
MLR	2.01187	5.93×10^{-03}	1.10355	3.82×10^{-01}	74.10969	3.75×10^{-02}
FC	2.01630	8.15×10^{-03}	1.16870	3.45×10^{-01}	74.31534	3.49×10^{-02}
EL	1.94925	2.54×10^{-02}	0.49043	7.25×10^{-01}	71.96257	6.54×10^{-02}

[a] n, kinetic exponent; k_0, pre-exponential factor (s^{-1}); E_a, activation energy (kJ mol^{-1}).
[b] Theoretical parameters: $n = 2$, $k_0 = 1.78482 \times 10^{08}$, $E_a = 77$ kJ mol^{-1}.
[c] er (x), relative error in the parameter x.

Table 2
Comparison of kinetic parameters for the Achar–Brindley–Sharp (ABS), multiple linear regression (MLR), Freeman–Carroll (FC) and Ellerstein (EL) methods in the 10–90% interval using 780 kinetic data points

	$n^{a,b}$	er $(n)^{c}$	$k_0 \times 10^{-08\ a,b}$	er$(k_0)^{c}$	$E_a^{a,b}$	er $(E_a)^{c}$
ABC	2.00	–	1.77629	4.78×10^{-03}	76.96786	4.17×10^{-04}
MLR	1.99987	6.73×10^{-05}	1.77290	6.68×10^{-03}	76.96216	4.91×10^{-04}
FC	1.99987	6.40×10^{-05}	1.77306	6.59×10^{-03}	76.96273	4.84×10^{-04}
EL	1.99984	7.77×10^{-05}	1.77237	6.97×10^{-03}	76.96167	4.98×10^{-04}

[a] n, kinetic exponent; k_0, pre-exponential factor (s^{-1}); E_a, activation energy (kJ mol^{-1}).

[b] Theoretical parameters: $n = 2$, $k_0 = 1.78482 \times 10^{08}$, $E_a = 77$ kJ mol^{-1}.

[c] er (x), relative error in the parameter x.

Table 3
LSM values vs. the number of points using the Achar–Brindley–Sharp (ABS), multiple linear regression (MLR), Freeman–Carroll (FC) and Ellerstein (EL) methods

LSM[a]	780	112	10
ABS	2.36×10^{-06}	2.61×10^{-05}	1.02×10^{-02}
MLR	8.20×10^{-08}	1.23×10^{-06}	8.91×10^{-03}
FC	5.90×10^{-05}	7.36×10^{-04}	9.44×10^{-01}
EL	1.12×10^{-04}	1.66×10^{-03}	$3.45 \times 10^{+01}$

[a] LSM, fit of the calculated curve with the simulated one.

and 3 show the constancy of the activation energy values obtained from the Achar–Brindley–Sharp, multiple linear regression and Freeman–Carroll methods for the same number of data points. The values given by these last three methods are quite different from those obtained with the Ellerstein method, when the number of points is decreased. For this last method, compared to the multiple linear regression method when using 10 kinetic data points, this represents a divergence of 2.90%. With the maximum points tested (780 points), this divergence decreases to 6.37×10^{-4}% (Table 2, Fig. 3) and the four methods tested seem appropriate for the determination of activation energy.

Similar conclusions can be drawn considering the relative error on kinetic order n vs. the number of points (Fig. 4). For the Achar–Brindley–Sharp method, n is not derived from calculations, but represents the value retained for the best correlation coefficient of the plot of the Arrhenius line. Incrementation by a value of 10^{-2} was retained to check the validity of this method in a reasonable computing time, so that the value 2.00 is found for a sufficient number of kinetic data points (Table 2). The Freeman–Carroll and multiple linear regression methods lead to very good accuracy when the number of kinetic data points is more than 100, but deviations are observed with Ellerstein's

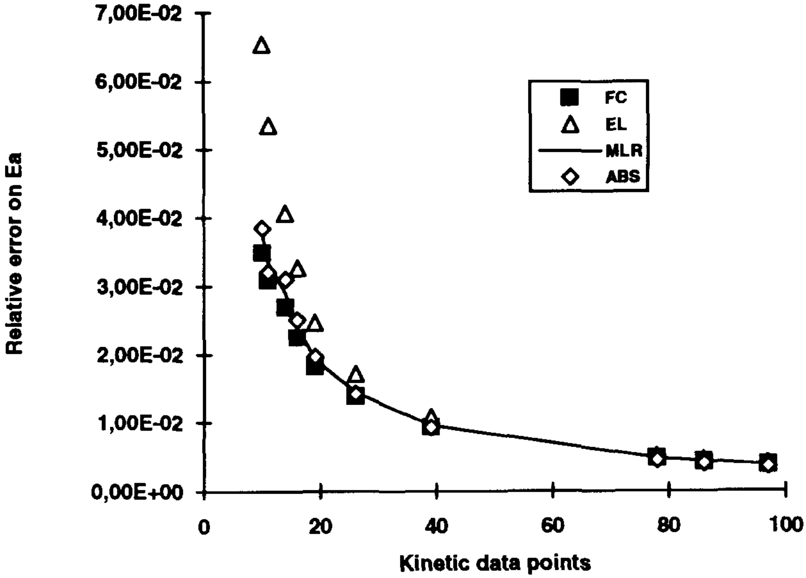

Fig. 2. Relative errors on the activation energy E_a vs. the number of kinetic data points from 10 to 97 for the Freeman-Carroll (FC), Ellerstein (EL), multiple linear regression (MLR) and Achar-Brindley-Sharp (ABS) methods.

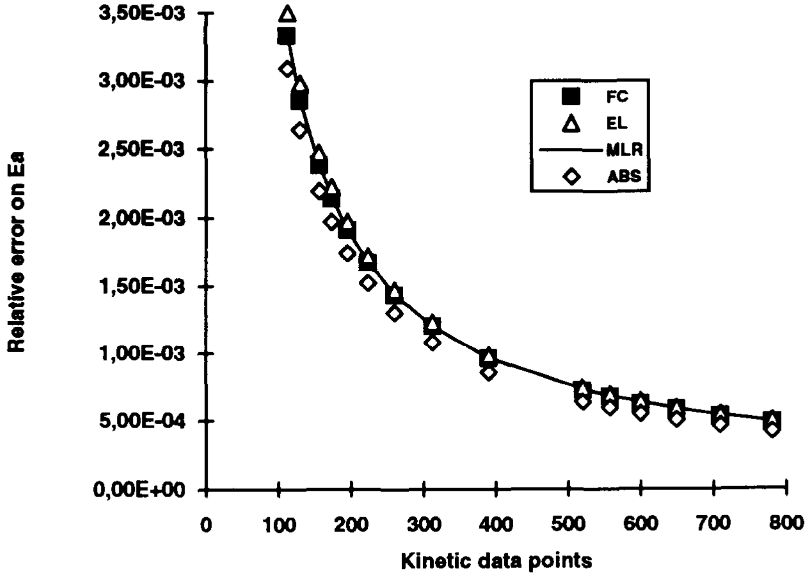

Fig. 3. Relative error on the activation energy E_a vs. the number of kinetic data points > 100 for the Freeman-Carroll (FC), Ellerstein (EL), multiple linear regression (MLR) and Achar-Brindley-Sharp (ABS) methods.

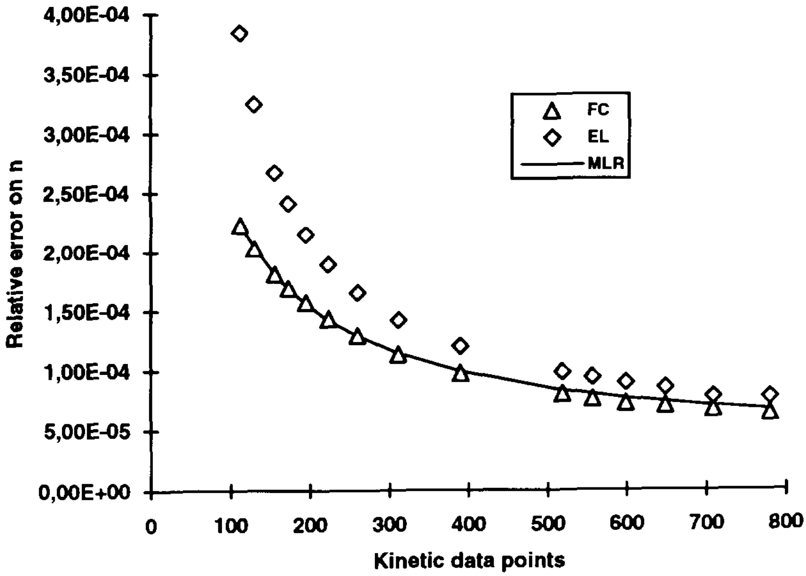

Fig. 4. Relative error on the kinetic order vs. the number of kinetic data points > 100 for the Freeman–Carroll (FC), Ellerstein (EL) and multiple linear regression (MLR) methods.

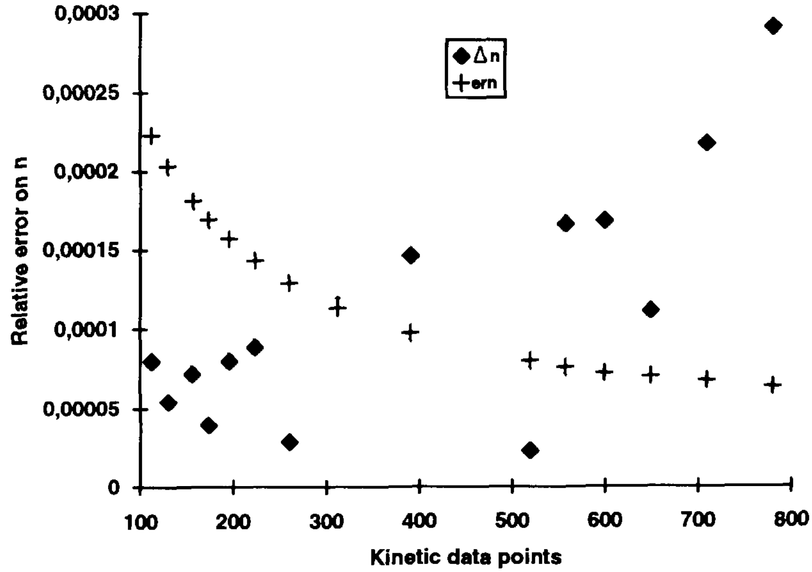

Fig. 5. Relative error on the kinetic order (er$n$) and Δn vs. the number of kinetic data points > 100 for the Freeman–Carroll (FC) method.

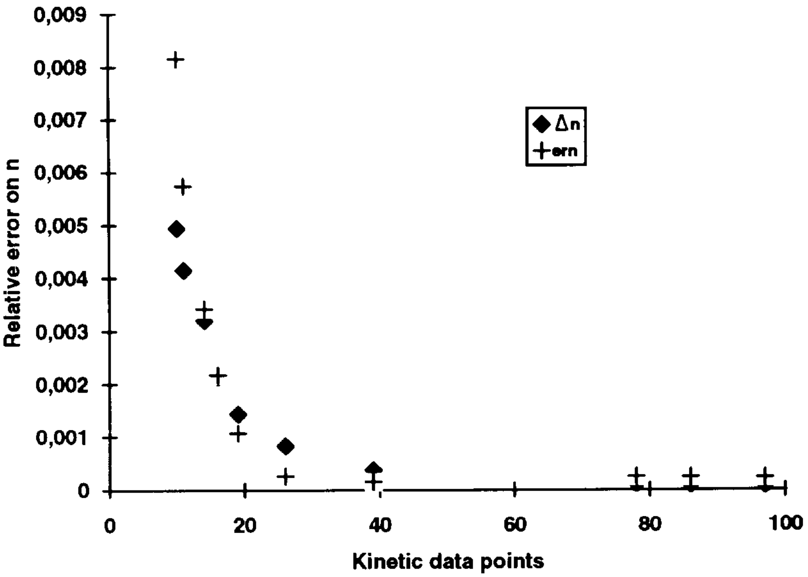

Fig. 6. Relative error on the kinetic order (er*n*) and Δ*n* vs. the number of kinetic data points < 100 for the Freeman–Carroll (FC) method.

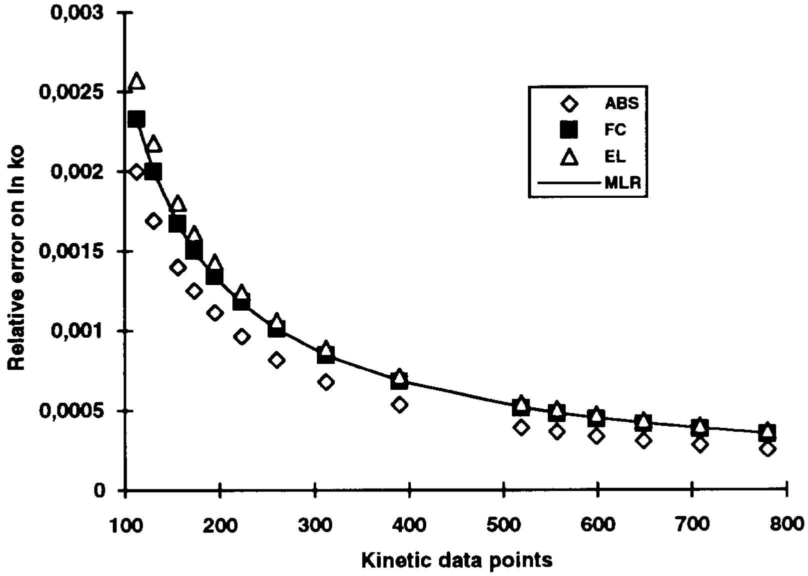

Fig. 7. Relative error on the logarithm of the pre-exponential factor vs. the number of kinetic data points > 100 for the Freeman–Carroll (FC), Ellerstein (EL), multiple linear regression (MLR) and Achar–Brindley–Sharp (ABS) methods.

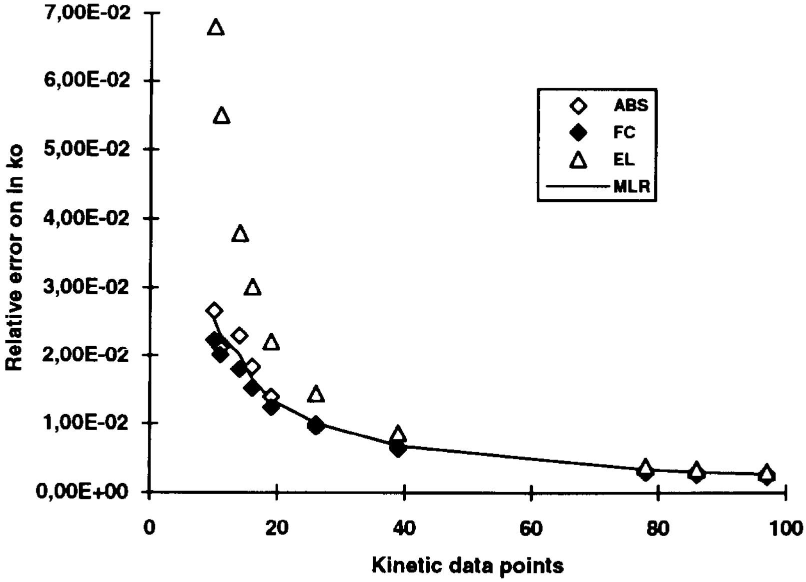

Fig. 8. Relative error on the logarithm of the pre-exponential factor vs. the number of kinetic data points < 100 for the Freeman–Carroll (FC), Ellerstein (EL), multiple linear regression (MLR) and Achar–Brindley–Sharp (ABS) methods.

method (Fig. 4). So the maximum value of this relative error on *n* is 2.54% and is obtained with Ellerstein's method using 10 points (Table 1).

For the Freeman–Carroll method, in addition to the relative error on the kinetic order *n*, we have computed Δn performed according to the method proposed by Jerez [17]. However, these two parameters are only correlated when the number of points is small (lower than 112, Figs. 5 and 6). For this last method, the relative error on the kinetic order *n* is never higher than 0.82%, which is low. Because evaluation of this parameter is very sensitive to the scatter of the plot of the Arrhenius lines [2], a later study with additional noise would be useful in order to reach any conclusion.

In the case of simulated data performed without noise, the accuracy of the logarithm of the pre-exponential factor ($\ln k_0$) is always correct, as for the other kinetic parameters. Relative errors on the pre-exponential factor have been computed instead of relative errors on the logarithm of the pre-exponential factor. This may be of interest because the LSM computation involves the evaluation of the pre-exponential factor. Of course, relative errors are magnified when taking the antilogarithm of the pre-exponential factor and this explains part of the differences observed in the LSM values for the Ellerstein method. So, relative errors on the pre-exponential factor are always the highest, especially when the number of kinetic data points is lower than 100. As an example, the relative error values (Table 1) are 72.5, 39.6, 38.2, 34.5% respectively for the Ellerstein, Achar–Brindley–Sharp, multiple linear regression and Freeman–Carroll methods, when using 10 points. The relative error on this parameter shows the general downward trend when the sampling rate is increased. For the more precise modeling (780 points, Table 2), the lowest relative error is obtained with the Achar–Brindley–Sharp method; similar values are found for the Freeman–Carroll, multiple linear regression and Ellerstein methods. In order to perform comparisons, Figs. 7 and 8 give the variations of the logarithm of the pre-exponential factor vs. the number of points. As an example, the extreme values for the Ellerstein method are 0.037 and 6.80% (0.035% and 2.53% for the multiple linear regression method).

In conclusion, the highest relative errors were obtained when using only 10 points with the Ellerstein method and were 6.54% for the activation energy, 2.54% for the reaction order, and 72.5% for the pre-exponential factor, leading to an LSM value of 34.5. In similar conditions, the Freeman–Carroll method led to a higher relative error on the reaction order but to a lower on the pre-exponential factor and activation energy. It must be noted that, in such a case, an LSM value of 0.94 is found with the Freeman–Carroll method, while the two other methods (MLR and ABS) led to LSM values near to 10^{-2}. However, this method led to the lowest relative error on n, with 780 points. These observations could explain why some results obtained with the Freeman–Carroll method, subject to criticism [17–20] and variants [17, 21, 22], matched the good accuracy in terms of kinetic parameters reported in the literature, and may at least explain the disagreement between these authors. In summary, the lowest relative error values were found for the highest number of points, and the variations for all the methods tested were: 0.04–0.05% for the activation energy; 0.48–0.70% for the pre-exponential factor (0.03–0.04% for its logarithmic form); 0.06–0.08% for the reaction order (and 0.002–0.494% for the Δn calculation applied to the Freeman–Carroll method).

LSM values were also computed [1] in order to evaluate here, as with experimental thermoanalytical curves, the ability of the mathematical model used to fit the simulated thermoanalytical curve. Furthermore for modeling purposes, it is interesting to test the reliability between the LSM and the accuracy of each kinetic model used. Fig. 9 shows a comparison between the LSM values obtained from the four different methods vs. the number of kinetic data points. As the number of kinetic data points increases, the quality of the curve-fitting increases with a factor decrease of the LSM of at least 10^{-4} from 10 to 780 kinetic data points (see Table 3). The higher values of LSM, thus the worst fit, are obtained with the Ellerstein method followed by the Freeman–Carroll method. We found very low values of LSM for the Achar–Brindley–Sharp and multiple linear regression methods, respectively 2.36×10^{-6} and 8.20×10^{-8} (Table 3 and Fig. 9) for 780 data kinetic points. For the two methods leading to the best fit, higher robustness vs. the lack of kinetic points is obtained with the multiple linear regression method, compared to the Achar–Brindley–Sharp method (using a computing step on n of 10^{-2}). It must be recalled that in this case, the computing step on the reaction order n was limited for practical reasons, and if n is computed with a six-figure precision, the LSM value decreases to 9.68×10^{-8} ($n = 1.999860$) with 780 kinetic data points.

Another drawback of the Ellerstein method is brought to light by the LSM variations vs. the number of points of Fig. 9, where the minimum value for LSM does

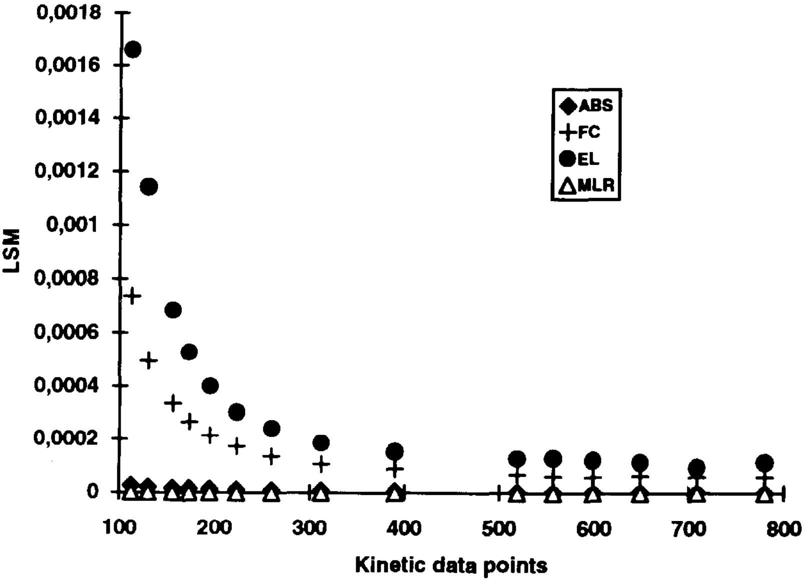

Fig. 9. LSM vs. the number of kinetic data points > 100 for the Freeman–Carroll (FC), Ellerstein (EL), multiple linear regression (MLR) and Achar–Brindley–Sharp (ABS) methods.

not exactly correspond to the maximum number of points as with the other methods, which confers an unpredicable character on this method (this may exist with the Freeman–Carroll method but with much less effect).

We verified the existence of very good correlations between LSM and the relative error on enthalpy, as well as between LSM and the relative error on the kinetic parameters, when the number of points is higher than 100, for the Achar–Brindley–Sharp, multiple linear regression, Freeman–Carroll and Ellerstein methods. So the accuracy of the fit for which the best results are given by the multiple regression method will depend on the accuracy of the evaluation of the enthalpy and on the kinetic parameters (especially the pre-exponential factor). Nevertheless, if we consider again Table 2, we can state that relative errors on the kinetic parameters are higher with the multiple linear regression method than with the Freeman–Carroll method, while the LSM value is higher for this last method. This may be explained in two ways: first, the "real" value for the kinetic parameters is not exactly known even in the case of simulations, so that use of the LSM parameter may be preferable to performing comparisons between the methods. Moreover, we think that this study brings to light the importance of the difference in the calculation of the kinetic parameters for the studied methods. For the Achar–Brindley–Sharp method, the reaction order retained is the one that gives the best linearization of the Arrhenius plot (involving E_a, n and $\ln k_0$), and then the activation energy and the logarithm of the pre-exponential factor are deduced. For the multiple linear regression method, the parameters (E_a, n and $\ln k_0$)

are computed by minimizing the residual between the data and the plot of the Arrhenius line. Indeed, in the Freeman–Carroll or Ellerstein methods, the reaction order and the activation energy are computed in a first step from one Arrhenius plot (involving E_a and n), and then $\ln k_0$ is deduced, with generally a lower correlation coefficient for the first step of the calculation and a correlation coefficient near to one for the second step [10]. The difference between these last methods and the Achar–Brindley–Sharp or multiple linear regression method, for a sufficient number of points in the case of simulated data, may result in the very good agreement between the kinetic parameters computed by the latter methods.

In order to evaluate the importance of the error on the enthalpy in kinetic computations performed in DSC, the following simulations were performed using the highest number of points retained for the integration of the thermoanalytical curve, i.e. the calculation of the enthalpy, with the possibility, for kinetic computations, of not using the same number of kinetic data points as the number of integrated points. The LSM computations were performed using the kinetic parameters obtained but taking into account all the integrated points. Comparison between rows 1 and 2 or 1 and 4 of Table 4, expresses the extent of the increase in the LSM values, i.e. the decrease in the accuracy of the simulations, when the sampling rate (Sr) is increased from 1 to 2 or 1 to 80. Comparison between rows 1 and 3 or 1 and 5 of Table 4 shows that the accuracy of the fit is comparable when the computation of kinetic parameters is performed using only 1 point every 2 points or 1 point every 80 points (except with Ellerstein's method). The same conclusions may be given in regard to the relative error on the pre-exponential factor (Table 5). Consequently, these findings show the importance of enthalpy computation in DSC study, because this parameter is used to compute the degree of conversion, and so imply, for kinetic studies, the performance of experimental DSC runs with the lowest sampling rate it is possible to record, according to the acquisition system of the apparatus used.

Table 4
Influence of the relative error on the enthalpy on the LSM values for the Achar–Brindley–Sharp (ABS), multiple linear regression (MLR), Freeman–Carroll (FC) and Ellerstein (EL) methods in the 10–90% interval

LSM[a]	ABS	MLR	FC	EL
1[b]	2.36×10^{-06}	8.20×10^{-08}	5.90×10^{-05}	1.12×10^{-04}
2[b]	5.13×10^{-06}	1.18×10^{-07}	8.79×10^{-05}	1.52×10^{-04}
3[b]	2.35×10^{-06}	8.16×10^{-08}	5.59×10^{-05}	1.02×10^{-04}
4[b]	1.02×10^{-02}	8.91×10^{-03}	9.44×10^{-01}	$3.45 \times 10^{+01}$
5[b]	2.39×10^{-06}	6.89×10^{-08}	1.05×10^{-05}	4.84×10^{-01}

[a] LSM, fit of the calculated curve with the simulated one.

[b] Row 1, sampling rate = 1; row 2, sampling rate = 2; row 3, sampling rate = 1, but only one point in every 2 has been retained for kinetic computations; row 4, sampling rate = 80; row 5, sampling rate = 1, but only one point in every 80 has been retained for kinetic computations.

Table 5
Influence of the relative error in the enthalpy on the relative error in the pre-exponential factor, for the Achar–Brindley–Sharp (ABS), multiple linear regression (MLR), Freeman–Carroll (FC) and Ellerstein (EL) methods in the 10–90% interval

er (k_0)[a] %	ABC	MLR	FC	EL
1[b]	0.48	0.67	0.66	0.70
2[b]	1.01	1.29	1.28	0.70
3[b]	0.48	0.67	0.66	0.73
4[b]	39.65	38.17	34.52	72.52
5[b]	0.49	0.66	0.65	58.99

[a] er (k_0), relative error in k_0.
[b] See footnote to Table 4.

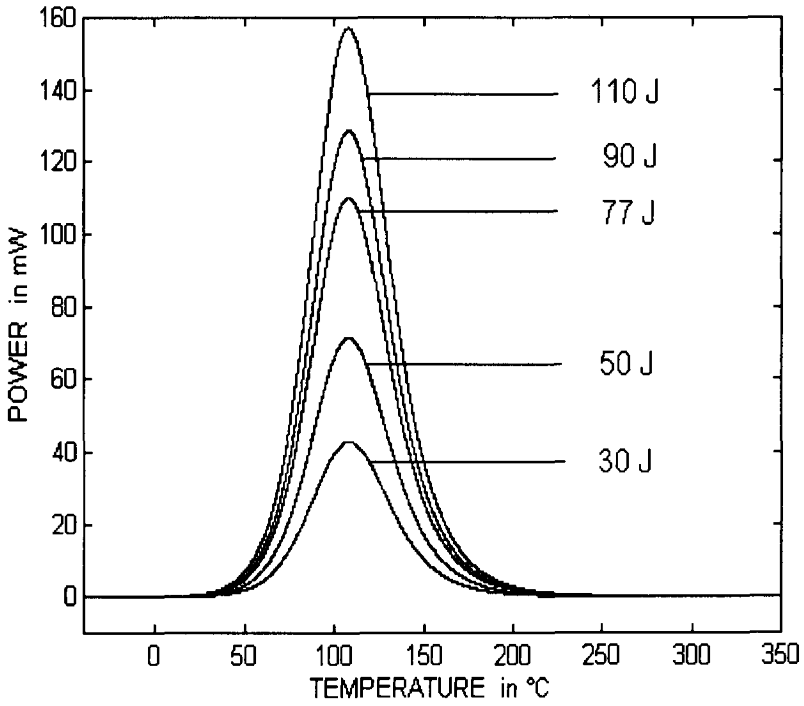

Fig. 10. Thermoanalytical curve shapes for various enthalpy values with the same kinetic parameters.

To proceed with the simulations, we may now consider the accuracy of the methods regarding various thermoanalytical curve shapes. Fig. 10 represents the different thermoanalytical curve shapes obtained for five enthalpy values ($\Delta H = 30, 50, 77, 90$ and 110 J) and constant kinetic parameters (those of the reference). The comparison of

LSM values clearly shows (Table 6) that, whatever the method used, these values are subject to an increase by a factor of 10 when increasing the enthalpy from 30 to 110 J. So the best fit was obtained for less sharp thermoanalytical curves (30 J, Table 6), as expected using kinetic data computed from the multiple linear regression and Achar–Brindley–Sharp methods. It is interesting to note that these increases in the total enthalpy of the transformation, keeping constant kinetic parameters, represent what should be observed for thermoanalytical curves recorded with various sample masses. The experimental variation shapes of such recordings are generally quite different, and this could be an interesting way of evaluating the thermal gradient effects, by means of simulations.

Another very interesting finding is that the relative errors in the kinetic parameters are constant, whatever the enthalpy value used in the simulation. For example, the relative errors in the activation energy values are respectively 4.1735×10^{-4}, 4.8×10^{-4}, 4.9145×10^{-4} and 4.98×10^{-4} for the Achar–Brindley–Sharp, Freeman–Carroll, multiple linear regression and Ellerstein methods for the same number of kinetic data points (780). These given relative errors indicate the precision of this constancy for each method, and we notice that only one number after the decimal point is constant for the Freeman–Carroll method. Because the relative error in the kinetic parameters is approximately constant for each method, one could expect constancy of the LSM values because the relative error found is a characteristic of the accuracy of the method used and is independent of the value of the enthalpy. This observation leads to some answers concerning the physical meaning of the LSM value when performing such comparisons. Accordingly, for comparing thermoanalytical curves of various amplitudes, we propose new ways of computing LSM which should be dimensionless. The first is called LSMR and is expressed as

$$\mathrm{LSMR} = \frac{1}{N}\sum_{i}\left(\frac{Y_{i,\mathrm{exp}} - Y_{i,\mathrm{comp}}}{Y_{i,\mathrm{exp}}}\right)^{2}$$

and the second

$$\mathrm{LSMr} = \frac{1}{N}\sum_{i}\left|\frac{Y_{i,\mathrm{exp}} - Y_{i,\mathrm{comp}}}{Y_{i,\mathrm{exp}}}\right|$$

We have found these LSM (LSMR and LSMr) values are constant for the Achar–Brindley–Sharp, multiple linear regression and Ellerstein methods for various enthalpies, but we found a few deviations for the Freeman–Carroll method (Table 6). However, as the LSMR values obtained are very small (10^{-8}–10^{-11}) it would be preferable to compute LSMr. Table 6 illustrates the constancy of the LSMr values vs. the enthalpy variation for the maximum of kinetic data points, compared to the LSM values. The use of LSMr could give an evaluation of each method's accuracy depending on the mathematical treatment as well as on the resolution of the peak when the relative error in the activation energy is not accessible, thus rejecting poor fit and methods sensitive to thermoanalytical curve shape variations, when various phenomena are to be compared.

Table 6
LSM and LSMr values for 780 kinetic data points vs. the enthalpy using the multiple linear regression (MLR), Achar–Brindley–Sharp (ABS), Freeman–Carroll (FC) and Ellerstein (EL) methods

ΔH[a]	ABS	MLR	FC		EL
	LMr[b] = 1.83×10^{-5}	LSMr[b] = 3.47×10^{-6}			LMr[b] = 1.25×10^{-04}
	LSM[c]	LSM[c]	LSM[c]	LSMr[b]	LSM[c]
30	3.58×10^{-07}	1.25×10^{-08}	8.94×10^{-06}	9.23×10^{-05}	1.71×10^{-05}
50	9.94×10^{-07}	3.46×10^{-08}	2.50×10^{-05}	9.26×10^{-05}	4.72×10^{-05}
77	2.36×10^{-06}	8.20×10^{-08}	5.90×10^{-05}	9.23×10^{-05}	1.12×10^{-04}
90	3.22×10^{-06}	1.12×10^{-07}	8.13×10^{-05}	9.27×10^{-05}	1.53×10^{-04}
110	4.81×10^{-06}	1.67×10^{-07}	1.19×10^{-04}	9.20×10^{-05}	2.29×10^{-04}

[a] ΔH, enthalpy value in J.

[b] LSMr, relative fit of the calculated curve with the simulated one.

[c] LSM, fit of the calculated curve with the simulated one.

4. Conclusions

This kinetic study on simulated thermoanalytical curves based on the kinetic homogeneous law shows that simulations may be used to minimize the difficulty of comparing kinetic methods and rejecting poor fitting models. The extent of the error that could result with a lack of data points has been evaluated, especially for the Ellerstein method, and thus care must be taken, especially for kinetic studies, in experimental design, with the choice of the sampling rate and with the number of kinetic data points used. However, the greater deviations from theoretical values were observed for the pre-exponential factor determination, whatever the method tested. The simulations have shown that the use of a precision of 10^{-2} for the reaction order with the Achar–Brindley–Sharp method is correct, but that the multiple linear regression method gives excellent results and is less time-consuming.

The greatest relative errors were obtained for ten kinetic data points with Ellerstein's method, leading to a high LSM value. The Freeman–Carroll method which has been the subject of criticism, gives accurate results for relative errors on the kinetic parameters, using completely simulated thermoanalytical curves, while, for modeling purposes, the LSM values are always higher than with the Achar–Brindley–Sharp and multiple linear regression methods. With the lowest number of kinetic data points, the Freeman–Carroll method leads to the highest relative error on the reaction order but to the lowest for the pre-exponential factor and the activation energy, while this method leads to the lowest relative error on the reaction order, with the highest number of kinetic data points. It is known that this method is sensitive to the scattering of the data, so a study with additional noise would be useful in order to make a final conclusion.

Good correlations exist between LSM and relative errors in kinetic parameter values, as well as the enthalpy, for a sufficient number of kinetic data points. This confirms the possible use of LSM when reference data are not available. The interpretation of the experimental results from different enthalpy values offers additional complexities to which the use of a relative LSM called LSMr could improve the ability of LSM to test the kinetic methods.

The simulation is promising in view of its success with theoretical data, and we also look forward to its employment in future work on filtering and deconvolution of DSC signals. The evaluation of relative errors in kinetic parameter values for each method given in this study will be useful in comparing these methods with more recent approaches used in the filtering of noisy signals. This numerical study was first performed using simulated thermoanalytical curves without additional noise but our wish is also to evaluate the robustness of each method in the case of additional noise.

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