Rate equations in the study of the DSC kinetics of epoxy-amine reactions in an excess of epoxy

Valery L. Zvetkov *, Rumen K. Krastev, Vassil I. Samichkov [1]

*Central Laboratory of Physical Chemical Mechanics, Bulgarian Academy of Sciences,
acad. G. Bontchev street, 1113 Sofia, Bulgaria*

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ABSTRACT

We show in this work that the heat flow signal as acquired applying DSC to systems in an excess of epoxy must be proportional to the rate of consumption of the excess component but not to the rate of reaction.

The rate equations reasoning from this finding have been analysed. According to the model, a DSC data set monitoring the reaction progress of an epoxy excess system must be identical to that exhibiting the reaction advance of the formulation at stoichiometry.

Experimental data confirming the proposed methodology have been presented. Both non-isothermal and isothermal DSC experiments support adequately the model.

The non-linear transform from the excess component measurement into the reaction rate expression has been also commented in the study from the point of view of the kinetics.

1. Introduction

The study of the reaction kinetics in epoxy-amine formulations has more than thirty years of history but it still remains an intriguing research field [1,2]. This is mainly due to the increasing range of applications of epoxy based products—structural adhesives, protective and transparency coatings for fibre optics, appliances in electronics, composite materials for the aerospace industry, etc.

From the point of view of the mass balance, the epoxy-amine addition is formally a bi-molecular stepwise reaction that takes place trough the opening of the oxirane rings of the epoxy component by hydrogen atoms of the amine component, as shown in Scheme 1.

According to this scheme each hydrogen atom belonging to either primary or secondary amine opens an epoxy ring to grow an amine-ended chain. If bi- or higher functional epoxies react with tri- or higher functional amines, then rigid and high T_g thermosetting polymers can be formed. The system consisting of a bi-functional epoxy and tetra-functional diamine is a typical example which has been often used for modeling purposes [3]. The primary amine sites in this system act as chain extenders while the secondary amines produce the branches.

The mechanism of the epoxy-amine reaction is more complex than depicted in Scheme 1. This is reflected in a reaction order that basically differs from two [4–7], but the mass balance problem solved in this work is based on the above presented elemental scheme.

The kinetics of the epoxy-amine addition has been studied by applying different physical chemistry methods to indirectly measure the concentration of reaction components. Most of the important early research in this respect has been reviewed in special issues of Advances in Polymer Science under the editorship of Dusek [8–12]. FTIR spectroscopy in the middle and near infrared region [9,13–29] and DSC [5–8,30–73] appear to be the most convenient techniques to investigate the epoxy-amine addition kinetics. There can be found in literature noteworthy studies performed with the aid of other sophisticated methods [74–78].

DSC is a direct differential method which outputs the heat flow signal [8]. This signal was trivially supposed to be proportional to the rate of reaction in its real time scale based on the physical analogy between the epoxy concentration and reaction heat. From this point of view, the DSC method possesses several advantages:

- the DSC cell can be considered as a batch mini-reactor with negligible heat dissipation able to measure with high accuracy both the rate of reaction and degree of conversion;
- the DSC instruments can operate in both isothermal and non-isothermal temperature mode allowing to apply different kinetic techniques in large temperature ranges; and

* Corresponding author. Tel.: +359 2 979 3907; fax: +359 2 703 433.
 E-mail addresses: zvetval@yahoo.com, zvetval@clphchm.bas.bg (V.L. Zvetkov).
 [1] Present address: University of Chemical Technology and Metallurgy, Department of Polymer Engineering, K. Ohridski Boulevard, 1756 Sofia, Bulgaria.
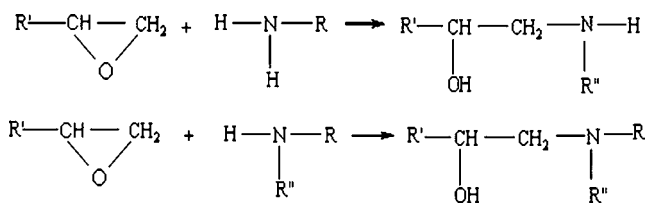
Scheme 1.

- the DSC method provides the variables required for solving the heat/mass transfer problems of real processes—heat flow and heat accumulation.

Additionally, the newly developed modulated temperature DSC's (MTDSC) are able to measure the heat capacity signal simultaneously and in real time with the heat flow signal [45–47,56–65]. In conjunction with the possibility to measure the T_g evolution in intermittent experiments during reaction advancement, the transfer of a liquid epoxy-amine mixture to a visco-elastic material can be studied successfully. Moreover, MTDSC can also make the distinction between a chemically controlled and diffusion-controlled reaction [46,47,56–64].

The main restriction of the DSC method consists in the possible inexactness of the epoxy concentration/reaction heat analogy, as detailed in the studies of Rozenberg [10] and Vinnik et al. [66]. The present work will discuss another restriction of the DSC method in field of the epoxy-amine addition kinetics, namely: the model description in an excess of epoxy.

We will show in this study that the heat flow signal as output from DSC applied to epoxy excess systems is linearly proportional to the rate of consumption of the excess component but not to the rate of reaction. The form of the rate equations reasoning from this finding is the main objective of this work.

The solution of the problem appears important since the curing of epoxy resins with amine hardeners is often performed for practical purposes in an excess of epoxy and in the presence of catalysts promoting other side reaction like the living polymerisation of epoxy rings and/or hydroxyl addition. We have to note, however, that an absence of a side reaction is desirable to solve the problem exactly.

2. Model fundamentals

2.1. Concentration profiles of the reaction components

Following Scheme 1, the concentrations of reaction components (at a reacted amount of the product x) and their current ratio can be expressed as:

$$a = a_0 - x \qquad e = e_0 - x \qquad R = \frac{a}{e} = \frac{(a_0 - x)}{(e_0 - x)} \tag{1}$$

where a and e are molar concentrations of amine hydrogen atoms and epoxy groups, a_0 and e_0 their initial values, and x the concentration of the currently achieved product, respectively; R denotes the current molar amine to epoxy ratio, the initial value of which can be determined at the reaction beginning, viz. $R_a = a_0/e_0$ (or $R_e = 1/R_a = e_0/a_0$).

In non-stoichiometric epoxy-amine mixtures, or $R_a \neq 1$, the final concentration of excess component, a_f or e_f, is not zero. E.g., in case of an epoxy excess mixture, a decreases from a_0 to 0, e decreases from e_0 to e_f, x increases from 0 to a_0, and R changes from R_a to 0.

Following Eqs. (1), it appears that the reaction rate can be determined from either excess or minority component data sets, since: $de/dt = da/dt = -dx/dt$.

However, the normalized derivatives, $d(a/a_0)/dt$ and $d(e/e_0)/dt$, extracted from the profiles (a/a_0) and (e/e_0) must be different. The initial point of both profiles is unity, but (a/a_0) vanishes zero while (e/e_0) approaches (e_f/e_0) at the end of reaction. The result is a time scale shift of (e/e_0) against (a/a_0) by the current normalized amine to epoxy ratio, R/R_a.

Having in mind the expressions of the product fraction definition, $\beta = (a_0 - a)/a_0 = (1 - a/a_0)$ and $\alpha = (e_0 - e)/(e_0 - e_f) = 1/R_a(1 - e/e_0)$, the corresponding normalized derivatives must be equal to: $d\beta/dt = -d(a/a_0)/dt$ and $d\alpha/dt = -1/R_a d(e/e_0)/dt$, respectively. According to these definitions, $d\beta/dt$ and $d\alpha/dt$ have to obey different rate equations, otherwise the profiles (a/a_0) and (e/e_0) must coincide. It is obvious that this is not true.

As the analysis in Appendix A and Appendix B shows, the profile (e/e_0) is being measured when applying DSC to systems in an excess of both amine and epoxy.

2.2. Enthalpy balance equation of the epoxy-amine addition

The physical analogy used in thermo-chemical measurements and thermo-kinetic studies of the epoxy-amine reactions relies on the relationship between the epoxy concentration and reaction heat, or (with minus sign) enthalpy release of the reacting systems [7,8,32–35,58].

This principle is not strictly applicable from a thermodynamic point of view, since the molar reaction enthalpy, ΔH^0, must be a sum of at least four terms [10], viz.

$$\Delta H^0 = \Delta H^e + \Delta H^a + \Delta H^{th} + \Delta H^s \tag{2}$$

where ΔH^e is the difference between the enthalpies of oxirane group atoms at two stages – prior the reaction and after its completion, ΔH^a the enthalpy difference of the co-reacting hydrogen atoms at the initial and final stage – amine group and hydroxyl group, respectively, ΔH^{th} the enthalpy difference accounting for all covalent and/or hydrogen bonding interactions between the polar groups existing in the monomer mixture and in the fully cured polymer, respectively; and ΔH^s the enthalpy of all side reactions that can take place together with the epoxy-amine addition; the superscript used denotes molar concentrations.

The analysis of the enthalpy balance has been performed in the review of Rozenberg [10]. Other noteworthy studies that theoretically and experimentally estimate the terms of the enthalpy balance formula are also available [32–35,41,58,66].

Considering this formula it has been proven that ΔH^e has the main contribution in the total enthalpy balance [10]. This is due to the dramatic exchange of the bond angles between the atoms forming the epoxy rings when the co-reactant breaks them, and the atoms become parts of simple σ-bonded hydrocarbon chains. Rozenberg has pointed out that the enthalpy release due to the transfer of hydrogen atoms from primary and secondary amine species to hydroxyl groups should not exceed one to several percents of the total enthalpy [10].

The debate about the magnitude of ΔH^{th} is important from the point of view of the kinetics [8,10,34,58,66]. Rozenberg has shown that the enthalpies of intermediate interactions are not negligible, but the ones prior to the reaction and those existing at the end of reaction appear to correlate. Thus, the dependence of ΔH^0 on stoichiometry has been observed to be nearly linear with epoxy conversion. In an absence of a side reaction, ΔH^0 has been determined in relatively narrow limits [7,8,10]:

$$\Delta H^0 = 106 \pm 8 \, \text{kJ mol}^{-1}$$

If the initial ratio of components is not unity, the starting amount of minority reactant fixes the maximal amount of the excess

reactant able to react. To determine the enthalpy release independent of R_a, it must be related against a unit amount of minority component.

Thus, the relationship between the molar enthalpy per unit amount of epoxy, ΔH^0, and enthalpy measured by DSC per unit mass of reactive mixture, ΔH_t, is given with [34]:

$$\Delta H^0 = \frac{\Delta H_t}{(\varphi_e / M_e) F(R_a)} \tag{3a}$$

where ΔH_t is the total reaction enthalpy expressed in kJ kg^{-1} reactive mixture, φ_e and M_e are the weight fraction and epoxy equivalent molar mass of the epoxy component, and $F(R_a)$ is some function of stoichiometry.

Assuming the above commented and usually accepted approximations, $F(R_a)$ must obey the below given simple form—Eqs. (3b) and (3c); in general, it should be more complex [10].

$$F(R_a) = R_a \quad R_a \leq 1 \text{ (epoxy excess)} \tag{3b}$$

$$F(R_a) = 1 \quad R_a \geq 1 \text{ (amine excess)} \tag{3c}$$

Thus, the fundamental relationships expressing the concentration/enthalpy release analogy assume the following mathematical form:

$$x = \frac{1}{\Delta H^0} \int_0^t \frac{d(\Delta H)}{dt} dt = \frac{\Delta H}{\Delta H^0} \tag{4}$$

$$e = \frac{1}{F(R_a)} \frac{\Delta H}{\Delta H^0} \tag{5}$$

$$e_0 = \frac{1}{F(R_a)} \frac{\Delta H_t}{\Delta H^0} \tag{6}$$

where ΔH is the current enthalpy of reaction, in kJ kg^{-1} reactive mixture.

The concentration/enthalpy release measuring analogy applied to the DSC signal yields:

$$\frac{dx}{dt} = \frac{1}{F(R_a)} \frac{d(\Delta H)}{\Delta H^0 dt} \tag{7}$$

We show in Appendix A that Eq. (7) is valid in case of an excess of amine. We also prove in Appendix B a non-linear relationship between the product and epoxy derivatives in case of an excess of epoxy. The resulting rate equations are commented in the next two subsections.

2.3. Rate equations of the epoxy-amine addition in an excess of amine

As the analysis in Appendix A shows, the heat flow signal of an amine excess system has to be linearly proportional to the rate of consumption of minority (epoxy) component being simply called the rate of reaction. Then, Eq. (7) takes the form:

$$\frac{dx}{dt} = -\frac{de}{dt} = \frac{d(\Delta H)}{\Delta H^0 dt} \tag{8}$$

Since ΔH^0 couples two normalizing quantities—e_0 and ΔH_t, Eq. (8) can be *rearranged in a dimension free form* [5–7], as it follows:

$$\frac{d(x/e_0)}{dt} = -\frac{d(e/e_0)}{dt} = \frac{d\alpha}{dt} = \frac{d(\Delta H)}{\Delta H_t dt} \tag{9}$$

where α is termed as degree of epoxy conversion.

These classical definitions [7] postulate that the product concentration, being equal to the epoxy and amine currently reacted fractions, can be expressed as:

$$x = e_0 - e = a_0 - a = \frac{1}{\Delta H^0} \int_0^t \frac{d(\Delta H)}{dt} dt = \frac{\Delta H}{\Delta H^0} \tag{10}$$

The initial and current concentrations of the reaction components are, respectively:

$$e_0 = \frac{\Delta H_t}{\Delta H^0} \quad \text{and} \quad e = \frac{\Delta H_t - \Delta H}{\Delta H^0} \tag{11}$$

$$a_0 = \frac{\Delta H_t R_a}{\Delta H^0} \quad \text{and} \quad a = R \frac{\Delta H_t - \Delta H}{\Delta H^0} = \frac{\Delta H_t R_a - \Delta H}{\Delta H^0} \tag{12}$$

and the current molar amine to epoxy ratio becomes:

$$R = \frac{\Delta H_t R_a - \Delta H}{\Delta H_t - \Delta H} = \frac{R_a - \alpha}{1 - \alpha} \tag{13}$$

The most popular description of the epoxy-amine reaction is based on the so-called model of Smith and Horie et al. [4,5]. Although it has been subjected to a reasonable criticism during the last few years [10,16,23,43,44,50,54,60–64,67,68,72], it has been still found operative in some cases [69–71]. The overall velocity equation of Horie et al. based on the well established hydroxyl promoted autocatalysis has the following mathematical form:

$$\frac{dx}{dt} = k_1' ea + k_1 [OH] ea \tag{14}$$

where [OH] might be either the total amount of all hydroxyl groups present in the reacting system [10,16,23] or the groups free of hydrogen bonding interactions [44,50,54,60-64,68,72].

Applying the epoxy concentration/enthalpy release analogy, the classical model of Smith and Horie et al. can be rewritten in an excess of amine by replacing the expressions for the concentration of epoxy, amine, and hydroxyl groups—see Eq. (10) through Eq. (12), viz.

$$\frac{dx}{dt} = k_1' \left(\frac{\Delta H_t}{\Delta H^0} - x \right) \left(\frac{R_a \Delta H_t}{\Delta H^0} - x \right)$$
$$+ k_1 x \left(\frac{\Delta H_t}{\Delta H^0} - x \right) \left(\frac{R_a \Delta H_t}{\Delta H^0} - x \right) \tag{15}$$

where the definition of x exactly reflects the epoxy concentration/enthalpy release analogy in an excess of amine.

It is also possible an entirely enthalpy description of the model in this case, viz.

$$-\frac{d(\Delta H_t - \Delta H)}{\Delta H^0 dt} = k_1' \frac{\Delta H_t - \Delta H}{\Delta H^0} \frac{\Delta H_t R_a - \Delta H}{\Delta H^0}$$
$$+ k_1 \frac{\Delta H}{\Delta H^0} \frac{\Delta H_t - \Delta H}{\Delta H^0} \frac{\Delta H_t R_a - \Delta H}{\Delta H^0}$$

Replacing the expression of ΔH^0, viz. $\Delta H^0 = \Delta H_t / e_0$, the latter is easily rearranged into the well known dimension free equation [6–8]:

$$\left(\frac{\Delta H_t}{\Delta H^0} \right) \frac{d\alpha}{dt} = k_1' \left(\frac{\Delta H_t}{\Delta H^0} \right)^2 (1 - \alpha)(R_a - \alpha)$$
$$+ k_1 \left(\frac{\Delta H_t}{\Delta H^0} \right)^3 \alpha (1 - \alpha)(R_a - \alpha) \tag{16}$$

Note that $\Delta H_t / \Delta H^0$ in the above equation represents the total amount of product or initial concentration of minority (epoxy) component. We have to emphasize again that Eq. (16) is a rearrangement of the enthalpy release equation and the normalization is a logic result of the rearrangement.

2.4. Rate equations of the epoxy-amine reaction in an excess of epoxy

The analysis of the concentration/enthalpy release analogy in case of an excess of epoxy is presented in Appendix B. We show

there the controversy reasoning from the DSC measuring principle and mass balance equation.

The analysis of a single DSC curve has yielded the expression of the normalized excess component variable being measured applying calorimetric techniques, viz.

$$\frac{e_0 - e}{e_0 - e_f} = \alpha = \frac{\Delta H}{\Delta H_t} = 1 - \frac{\Delta H_r}{\Delta H_t} = 1 - \alpha' \tag{17}$$

where ΔH_r denotes the currently remaining enthalpy.

The variable α in Eq. (17) must obey the same law as the minority component variable:

$$\frac{a_0 - a}{a_0} = \beta = \frac{\Delta H}{\Delta H_t} = 1 - \frac{\Delta H_r}{\Delta H_t} = 1 - \lambda \tag{18}$$

On the other hand, the analysis of the time independent residual enthalpy data has show a non-linear relationship between the epoxy concentration and reaction enthalpy, viz.

$$\frac{e}{e_0} = \frac{R_a}{R} \frac{\Delta H_r}{\Delta H_t} = \frac{R_a}{R}\left(1 - \frac{\Delta H}{\Delta H_t}\right) \tag{19}$$

Note that Eq. (19) is a rearrangement of the normalized product quantity. As the analysis in Section 2.1 implies, the time scale of minority component quantity, $(a/a_0) = -(x/a_0)$, must differ from that of the enthalpy measurement, $(e/e_0) = \Delta H/\Delta H_t$, by the ratio R/R_a.

Hence, the two derivatives must be coupled through the proportionality relation:

$$\frac{d(x/a_0)}{dt} = -\frac{d(a/a_0)}{dt} = -\frac{R_a}{R}\frac{d(e/e_0)}{dt} = \frac{R_a}{R}\frac{d(\Delta H)}{\Delta H_t dt} \tag{20}$$

The above relationship means that the ratio of derivatives $d(1 - e/e_0)/dt$ and $d(1 - a/a_0)/dt$ yields a relationship between the model functions expressing them, as shown in Appendix B. Two corollaries reason from the last equation.

1. The definition of reaction rate (in the time scale of the enthalpy measurement) means implicit multiplication of Eq. (20), as well as the model function, by R/R_a. Then, following the model of Smith and Horie et al. one can obtain:

$$\frac{d(\Delta H_t - \Delta H)}{\Delta H^0 dt} = \frac{R}{R_a}\left[k_1' \frac{\Delta H_t - \Delta H}{\Delta H^0} \frac{\Delta H_t - \Delta H}{R\,\Delta H^0}\right.$$
$$\left. + k_1 \frac{\Delta H}{\Delta H^0} \frac{\Delta H_t - \Delta H}{\Delta H^0} \frac{\Delta H_t - \Delta H}{R\,\Delta H^0}\right]$$

This equation can be simplified to:

$$-\frac{d\,\Delta H}{\Delta H^0\, dt} = \frac{k_1'}{R_a}\left(\frac{\Delta H_t - \Delta H}{\Delta H^0}\right)^2 + \frac{k_1}{R_a}\frac{\Delta H}{\Delta H^0}\left(\frac{\Delta H_t - \Delta H}{\Delta H^0}\right)^2$$

and further rearranged into the below presented dimension free form, viz.

$$\left(\frac{\Delta H_t}{\Delta H^0}\right)\frac{d\alpha}{dt} = k_1'\left(\frac{\Delta H_t}{R_a\,\Delta H^0}\right)\left(\frac{\Delta H_t}{\Delta H^0}\right)(1 - \alpha)^2$$
$$+ k_1\left(\frac{\Delta H_t}{R_a\,\Delta H^0}\right)\left(\frac{\Delta H_t}{\Delta H^0}\right)^2\alpha(1 - \alpha)^2 \tag{21}$$

where the current amine to epoxy ratio in case of an excess of epoxy must be:

$$R = \frac{\Delta H_t - \Delta H}{\Delta H_t/R_a - \Delta H} \tag{22}$$

Thus, the appearance of the DSC curves of an epoxy excess system must be similar to that of the formulation at stoichiometry, meaning that the effect of the initial amine to epoxy ratio would

not be evident. We will demonstrate this finding later in this work, as well as in our next study on the kinetics of DGEBA with DETA in an excess of epoxy. We have to also note the change of the dimension free rate constants in Eq. (21) with the change of stoichiometry.

2. One can renormalize the enthalpy (or excess component) measurement into minority component data according to Eq. (20). The derivation of the explicit renormalizing formula can be found in Appendix B, viz.

$$\frac{d[\ln(1 - \beta)]}{d[\ln(1 - \alpha)]} = \frac{1}{R} \tag{23}$$

Hence, one can be describe the autocatalytic model of Smith and Horie et al. in an epoxy excess system following the equation:

$$\frac{d\beta}{dt} = k_1'\left(\frac{\Delta H_t}{\Delta H^0}\right)(1 - \beta)(1/R_a - \beta)$$
$$+ k_1\left(\frac{\Delta H_t}{\Delta H^0}\right)^2 \beta(1 - \beta)(1/R_a - \beta) \tag{24}$$

where the expression of R after the renormalization must be identical to Eq. (22), viz.

$$R = \frac{1 - \beta}{1/R_a - \beta} \tag{25}$$

The renormalization according to Eq. (23) is simple, namely:

- the original heat flow data set must be converted into the dimension free form, viz. $d\alpha/dt = d(\Delta H/\Delta H_t)dt$;
- the integral curve $\alpha = f(t)$ needs to be constructed, as well;
- the current value of R has to be determined according to Eq. (22);
- multiplying $\Delta\ln(1 - \alpha)$ by $1/R$ yields $\Delta\ln(1 - \beta)$, and β can be calculated afterwards;
- the time derivative of β gives the remaining variable required to solve Eq. (24).

It seems at a first glance that the heat flow signal as derived in an excess of epoxy does not correspond to the reaction rate thus defined. However, this is not true if the former will be calculated in the exactly inverse order, namely:

- the concentration of amine component has to be calculated by solving numerically the product rate equation;
- the concentration of epoxy component obtainable using the mass balance equation and its normalized time derivative $d(e/e_0)/dt$ have to determined in the second step; and
- the heat flow signal must be calculated in its real time scale by obeying the below given normalized equation:

$$\frac{d(\Delta H)}{dt} = -\Delta H_t \frac{d(e/e_0)}{dt} = \Delta H_t \frac{d\alpha}{dt} \tag{26}$$

Performing the simulation in such a manner, the change of the time scale is being done implicitly when normalizing the (e/e_0) data, having in mind that $d(a/a_0)/d(e/e_0) = R/R_a$.

3. Experimental

The first epoxy resin we used in this work was a commercial product based on diglycidyl ether of bisphenol-A, DGEBA. It was synthesized at the factory Lakprom-Sofia under the name D-450 epoxy. The amine hardener we used for this resin was diethylene triamine (DETA, 97 % pure grade reactant, supplied by Fluka). The main impurity percentage of DETA was ethylene

diamine. Both components of this system were applied without further purification. The weight equivalent molar mass of D-450, M_w, was determined within 395–400 g mol^{-1} applying different physical chemistry methods. In comparison, M_w of the model resin of Dow Chemical (DER-332) was found out within 348–350 g mol^{-1} using the same methods. The value of M_w = 398 g mol^{-1} has been accepted corresponding to a composition of 10.5 PHR of DETA at stoichiometry. The experimental method we used in this part of the study was conventional non-isothermal DSC. A PerkinElmer DSC-2C instrument equipped with an argon purge gass device (20 mL min^{-1}) and refrigerating system (Intercooler II) was interfaced to 3600 Data Station through the standard data acquisition and analytical software. The instrument was regularly calibrated using In and Zn standards paying special attention on the baseline performance. The experimental data collected in the controlling computer were transferred in an IBM compatible PC, and the analysed was performed using MS Excel.

The second epoxy resin we used in this study was the well-known commercial product of Shell (Epon-825, M_w = 360 g mol^{-1}) [62]. The amine hardener for this resin was methylene dianilide (MDA, M_w = 198 g mol^{-1}, purity = 99 %) supplied from Aldrich.

A TA Instruments 2920 DSC with Refrigerated Cooling System (RCS) was used for the DSC experiments of the formulations Epon-825 with MDA. Samples ranging from 5 to 10 mg were measured using hermetic crucibles. Helium was used as a purge gas (25 mL min^{-1}) and Indium and cyclohexane were used as temperature and enthalpy calibrants, respectively. Isothermal MTDSC measurements were obtained by quickly heating (at 30 K min^{-1}) the reactive mixture to the cure temperatures of interest. The description of the techniques and materials can be found in more detail in Refs. [51,52,61,62].

4. Results and discussion

4.1. The curing reaction of DGEBA with DETA

The curing reaction of different DGEBA–DETA formulations has been studied mainly in non-isothermal regime at a heating rate of 10 K min^{-1}. Test experiments have been carried out in isothermal DSC mode within curing temperatures of 40–60 °C (T_c = 313–333 K), and in programmed temperature DSC mode ranging within 1 and 10 K min^{-1}. The initial reactant ratio has been varied from R_a = 0.571 to R_a = 1.333 (6–14 PHR of DETA).

The DSC curves obtained at 10 K min^{-1} have exhibited a main exotherm started at a nearly constant initial temperature of 20 °C (T_i = 293 K) for all formulation being studied and ended at a final temperature of 195 °C (T_f = 468 K) for the system at stoichiometry; T_f of all off-stoichiometric formulations has been found lower than 195 °C in an excess of both amine and epoxy. A second well resolved exotherm of the DSC curves which started at approximately 210 °C (T_s = 483 K) has been observed for all epoxy excess specimens. It can
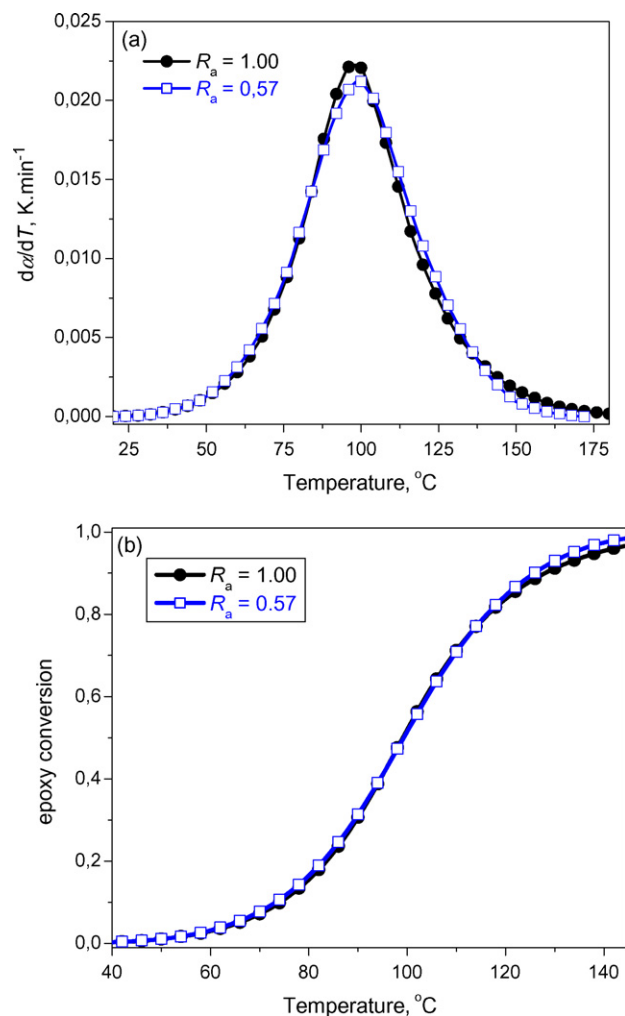

Fig. 1. Non-isothermal normalized curing curves for the reaction of DGEBA with DETA in an excess of epoxy at dT/dt = 10 K min^{-1}: (a) dα/dT versus T; and (b) α versus T. The values of the initial amine to epoxy ratio are labeled in the figures.

be attributed to a side reaction—hydroxyl addition and/or homopolymerization of epoxy rings. Nearly proportional shift of T_p, T_f, and T_s has been established with the change of scanning rate.

The data which characterise the main curing peak extracted at dT/dt = 10 K min^{-1} for all formulations under study are summarized in Table 1.

The normalized DSC curves for the system of DGEBA with DETA which cover the entire investigated range of R_a in an excess of epoxy at 10 K min^{-1}, dα/dt = d(ΔH)/ΔH_tdt versus T, are shown in Fig. 1a and b presents the integral plot of α versus T. The experimentally

Table 1
Peak maximum characteristics of the DSC curing curves in dependence of the initial reactant ratio for the reaction of a DGEBA based epoxy (M_w = 398 mol kg^{-1}) with DETA at dT/dt = 10 K min^{-1}

| PHR	$R_a = a_0/e_0$	ΔH	Characteristic temperatures				Characteristics at T_p	
		kJ kg^{-1}	T_i, K	T_p, K	T_f, K	T_s, K	α_p	(dα/dt)$_p$, K^{-1}
6.0	0.571	294.4	293	372.3	443	483	0.494	0.0212
7.0	0.667	337.4	293	371.9	445	483	0.489	0.0213
9.0	0.857	423.0	293	371.5	459	483	0.479	0.0221
10.0	0.952	468.7	293	371.3	463	483	0.476	0.0221
10.5	1	489.1	293	370.9	468	483	0.468	0.0223
12.0	1.143	505.6	293	369.8	451	–	0.520	0.0244
13.0	1.238	507.8	293	369.4	441	–	0.530	0.0253
14.0	1.333	503.8	293	369.0	423	–	0.555	0.0273
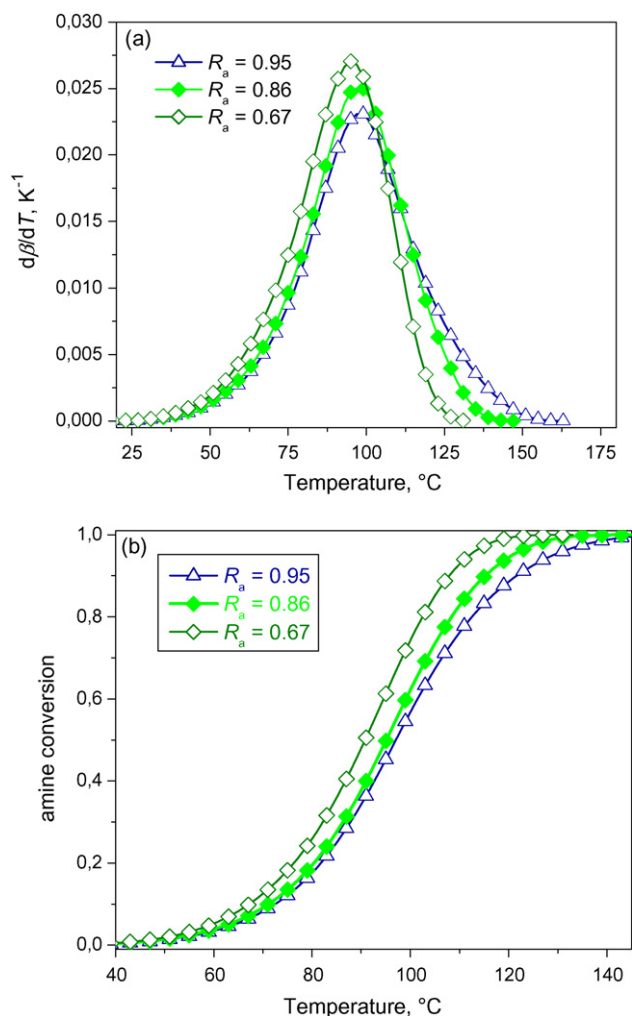
Fig. 2. Non-isothermal renormalized curing curves for the reaction of DGEBA with DETA in an excess of epoxy at $dT/dt = 10\,K\,min^{-1}$: (a) $d\beta/dT$ versus T; and (b) β versus T. The values of the initial amine to epoxy ratio are labeled in the figures.

Table 2

Peak maximum characteristics of the renormalized rate curves in dependence of the initial reactant ratio for the reaction of a DGEBA based epoxy ($M_w = 398\,mol\,kg^{-1}$) with DETA at $dT/dt = 10\,K\,min^{-1}$

PHR	$R_e = e_0/a_0$	Characteristic temperatures			Characteristics at T_p	
		T_i, K	T_p, K	T_f, K	β_p	$(d\beta/dT)_p$, K^{-1}
10.5	1	293	370.9	467	0.468	0.0223
10.0	1.05	293	370.8	441	0.488	0.0231
9.0	1.17	293	370.6	428	0.529	0.0251
7.0	1.50	293	368.5	411	0.591	0.0271
6.0	1.75	293	367.0	407	0.603	0.0277

ology we propose to study the DSC kinetics of the epoxy-amine addition in an excess of epoxy is probably correct.

Besides of the stoichiometry effect, the graphical plots in Fig. 2 and Fig. 3 quantitatively predict the reaction delay (or acceleration), thus accounting the self-dilution effect of reacting groups by the inert parts of their molecules.

We will discuss the kinetics in the system DGEBA with DETA based on Eq. (21) in one of our next studies but the main results derived in this work can be reported. The tri-molecular autocatalytic model with a single set of kinetic parameters, $E_a = 58\,kJ\,mol^{-1}$, has been found out to describe well the non-isothermal DSC kinetics in the system DGEBA with DETA in an excess of both amine
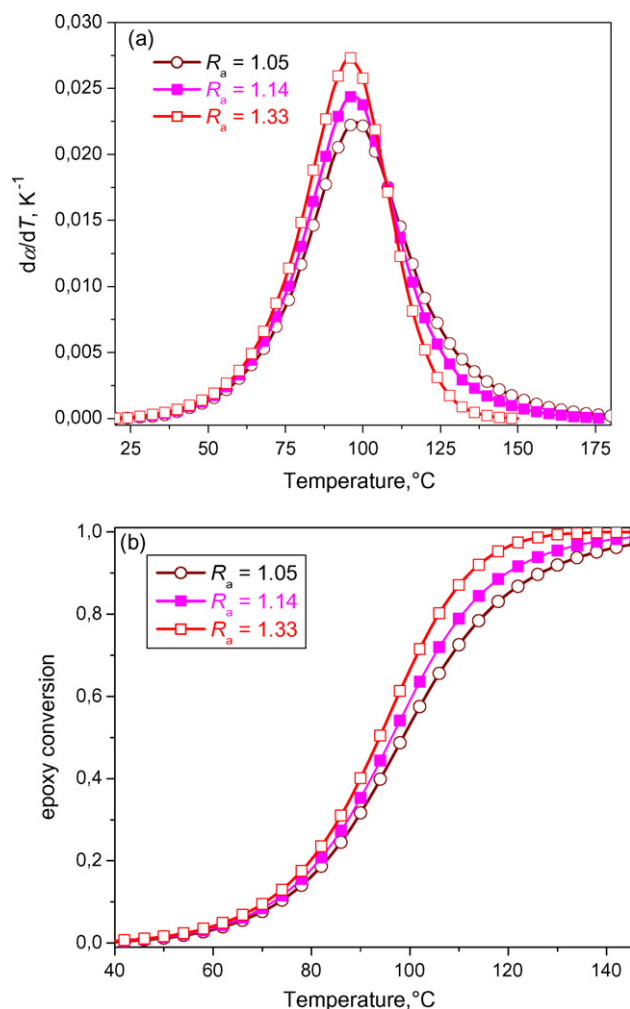
derived identical plots for any epoxy excess formulation within the listed R_a values almost coincide with that depicted in Fig. 1. The influence of stoichiometry on the reaction progress has been observed at high degrees of conversion, where T_f decreases with the decrease of R_a.

The data represented in a graphical form in Fig. 1 and summarized as numerical values in Table 1 appear to confirm the transform according to Eq. (21). As the model predicts, the rate signal of an epoxy excess formulation must obey an equation similar, although not identical with the equation describing the reaction rate of the system at stoichiometry.

Following the procedure explained in Section 2.4, the renormalized rate curves in terms of product, $d\beta/dt$, have been calculated. They are presented in Fig. 2a. The parameters which characterise $d\beta/dt$ curves are listed in Table 2. The normalized curves of the amine excess specimens, $d\alpha/dt$, are depicted in comparison in Fig. 3a. The corresponding integral curves, β versus T (epoxy excess) and α versus T (amine excess), are shown in Figs. 2b and 3b, respectively.

The comparison of Figs. 1 and 2 elucidate the fact that the product growth functions α and β must obey different rate equations. In agreement with the basic laws in the kinetics, the data in Fig. 2 and Fig. 3 evidences the effect of stoichiometry in an excess of both amine and epoxy. It again appears that the renormalizing method-

Fig. 3. Non-isothermal normalized curing curves for the reaction of DGEBA with DETA in an excess of amine at $dT/dt = 10\,K\,min^{-1}$: (a) $d\alpha/dT$ versus T; and (b) α versus T. The values of the initial amine to epoxy ratio are labeled in the figures.

and epoxy. Based on isothermal experiments exhibiting deviations from non-isothermal model prediction, it has been concluded that the model of Smith and Horie et al. probably masks a more complex mechanism [51,52,55]. In spite the approximate validity of the latter, the experiment confirms adequately the developed methodology.

4.2. The curing reaction of DGEBA with MDA [62]

The non-isothermal DSC curing curves of different formulations of DGEBA with MDA are presented in Fig. 4 in comparison with the curve of the formulation at stoichiometry. The corresponding normalized curves are shown in Fig. 5. The non-isothermal DSC curing peak characteristics are given in Table 3.

The analysis of the data listed in Table 3, as well as their graphical representation in Fig. 4 and Fig. 5, indicates a principal agreement with the data we have already commented:

• the curve in Fig. 5a exhibiting the reaction progress in an amine excess formulation of DGEBA with MDA accounts simultaneously for two effects—effect of stoichiometry and self-dilution effect; the former is well evident;
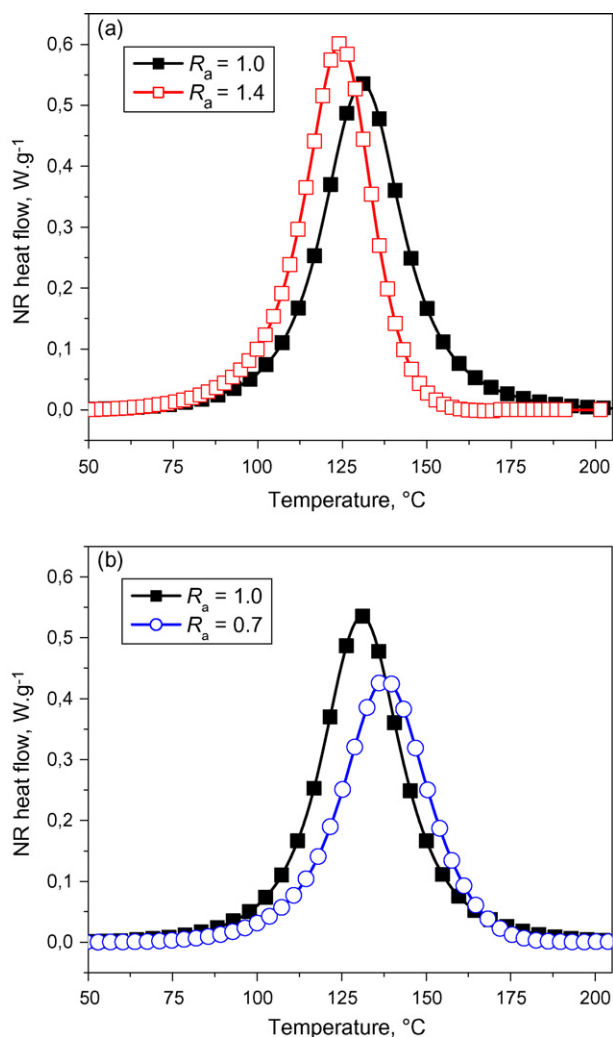

Fig. 4. Experimental non-isothermal heat flow curves of off-stoichiometric formulations of DGEBA with MDA compared with the curve of the formulation at stoichiometry [62]: (a) amine excess; (b) epoxy excess. dT/dt = 2.43 K min^{-1}.
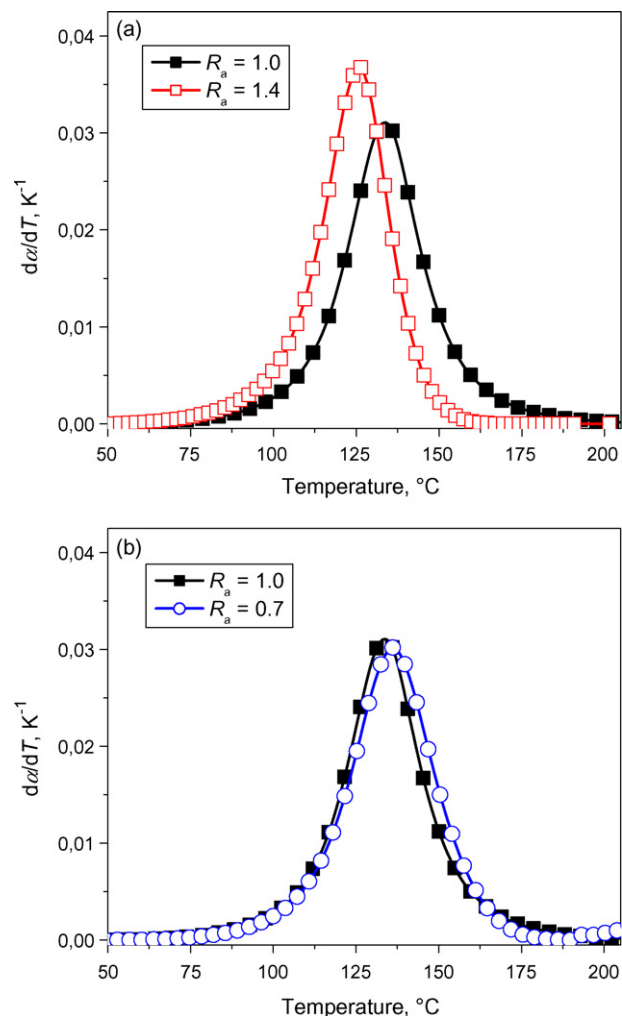

Fig. 5. Non-isothermal curves rate of epoxy conversion versus temperature for the reaction of DGEBA with MDA compared with the curve of the formulation at stoichiometry [62]: (a) amine excess; (b) epoxy excess. dT/dt = 2.43 K min^{-1}.

• the curve in Fig. 5b depicting the reaction advance in an epoxy excess formulation of DGEBA with MDA confirms the transform procedure according to Eq. (21); due to the self-dilution effect, this curve is normally delayed compared to that of the formulation at stoichiometry but its appearance is close to the latter; note that Eq. (21) is a particular case of the transform from the product rate equation into the excess component expression; the reaction model based on these data has been found out more complex [62];

A similar picture to that shown in Fig. 4 and Fig. 5 has been observed for the reaction of PGE with aniline, although the analysis of the isothermal data on this system confirms only qualitatively the proposed methodology.

Table 3
Peak maximum characteristics of the DSC curing curves in dependence of the initial reactant ratio for the reaction of a DGEBA based epoxy (M_w = 360 mol kg^{-1}) with MDA at dT/dt = 2.43 K min^{-1} [62]

$R_a = a_0/e_0$	Characteristic temperatures				Characteristics at T_p	
	T_i, K	T_p, K	T_f, K	T_s, K	α_p	(dα/dT)$_p$, K^{-1}
0.7	323	412.4	463	463	0.504	0.0301
1.0	323	406.1	503	–	0.487	0.0303
1.4	323	398.9	443	483	0.561	0.0368

Table 4
Characteristics of the DSC curing curves in dependence of the initial reactant ratio for the reaction of a DGEBA based epoxy ($M_w = 360$ mol kg^{-1}) with MDA at approximately 99 °C (372 K)[a] [62]

$R_a = a_0/e_0$	$R_e = e_0/a_0$	T_c, K	$(d\alpha/dt)_0$, s^{-1}	Parameters at t_p		
				t_p, min	α_p	$(d\alpha/dt)_p$, s^{-1}
$R_a = 1.40$		371.5	0.893×10^{-4}	27.0	0.496	5.62×10^{-4}
$R_a = 1.00$	$R_e = 1.00$	373.0	0.660×10^{-4}	32.3	0.426	3.60×10^{-4}
	$R_e = 1.43$	371.8	0.737×10^{-4}	41.2	0.432	2.67×10^{-4}
	$R_e = 2.50$	371.5	0.489×10^{-4}	66.3	0.444	1.60×10^{-4}

[a]The actual curing temperatures, T_c (in K), of all formulations are given in the table.

We have to point out that the non-isothermal curing peaks of DGEBA with MDA epoxy excess formulations has also exhibited a small but distinct second exotherm, which can be again ascribed to a side reaction. It starts at nearly 190 °C ($T_s \approx 463$ K), set as T_f of the main curing peak. Having in mind the temperature shift due to the scanning rate, $T_s \approx 463$ K detected for the system DGEBA with MDA at ≈ 2.5 K min^{-1} correlates well with $T_s \approx 483$ K observed for the system DGEBA with DETA at 10 K min^{-1}. It can be concluded that nearly equal kinetic parameters govern the side reaction in both reactive mixtures.

The side reaction can be either homo-polymerization of epoxy rings or hydroxyl addition. The topological restrictions in the network-forming polymer make the former improbable at high degrees of conversion, while the large excess of hydroxyl groups advantages the latter. The energetically favoured amine addition – in the absence of an external catalyst – must be also topologically restricted at its final stage. The fraction of epoxy groups unable to find their amine hydrogen partners has been estimated theoretically to approximately 0.04 [12]. It is noteworthy that the enthalpy measured above T_f from the curing curve of an epoxy excess formulation (against ΔH_t of the main exotherm) is of the same order.

The presence of an even small amount of product obtained via a side reaction alters the renormalization at the reaction completion since the calculated values of R become unreliable. Fortunately, this is not the case for all formulations studied in this work using non-isothermal DSC experiments, e.g. the second exotherm of the non-isothermal epoxy excess curing curve depicted in Fig. 5b appears distinctly resolved.

The standard mathematical procedure followed in the present study indicates that the last few points must be excluded from the analysis because of the uncertainty of the model at the reaction end, i.e. division of zero by zero.

Additionally, the analysis of the renormalizing equation shows that the model functions must contain multipliers proportional to the concentration of both epoxy and amine groups in a clear form. This might be also not true for the complex models. All above listed facts make the renormalizing formula approximate. Hence, the other possibility to investigate the epoxy-amine addition kinetics according to our model is preferable.

The test of the proposed methodology on the system DGEBA with MDA has been also carried out based on isothermal DSC experiments. The calculated DSC peak characteristics at $t = 0$ and $t = t_p$ of the isothermal DSC curves for the formulation of DGEBA with MDA are summarized in Table 4.

Similarly to the data obtained in non-isothermal DSC mode which visually evidence the effect of stoichiometry, the numerical isothermal data given in Table 4 also appear to support our hypothesis concerning this effect.

Varying $R_e = 1/R_a$ in an excess of epoxy from $R_e = 1$ to $R_e = 2.5$ causes an increase of α_p—from $\alpha_p = 0.426$ (at $R_e = 1$) to $\alpha_p = 0.444$ (at $R_e = 2.5$). Considerably less variance of R_a in an excess of amine, within $R_a = 1$ and $R_a = 1.33$, strongly increases α_p value—from $\alpha_p = 0.426$ (at $R_a = 1$) to $\alpha_p = 0.496$ (at $R_a = 1.33$). As one can establish, the difference is noticeable.

5. Conclusions

The analysis performed in this work shows that the heat flow signal as acquired applying DSC in the study of the epoxy-amine addition must be proportional to the time derivative of the normalized epoxy concentration.

The classical description of a heat flow curve obtained for an amine excess system yields a dimension free rearrangement of the product rate equation. As it is known, the equation with respect to the product derivative is the fundamental differential equation in the kinetics.

Following the measuring analogy between the epoxy concentration and reaction heat, we prove that the heat flow signal as acquired applying DSC to systems in an excess of epoxy does not obey the product rate equation. It obeys an equation the model function of which must be multiplied by the current normalized amine to epoxy ratio, R/R_a.

Experimental data confirming this finding are presented in this study. According to the model, the appearance of a DSC curve obtained for an epoxy excess system must be similar to that describing the reaction progress of the formulation at stoichiometry. The presented non-isothermal heat flow curves for two reactions studied in an excess of epoxy, DGEBA with DETA and DGEBA with MDA, confirm adequately this proposal.

The peak maximum characteristics calculated from isothermal DSC experiments on the reaction of DGEBA with MDA in dependence of stoichiometry are also in close agreement with the model prediction.

We have to note finally that a similar problem to that solved in this work probably exists for other formally bi-molecular reactions.

Appendix A. Analysis of the reaction rate definition in an excess of amine

To derive the correct expressions for the reaction rate, we will compare the hypothetic signal which can be output using an ideal quasi-isothermal adiabatic calorimeter, QIAC, and the signal originally acquired using existing DSC equipment.

Having a single data set from a QIAC experiment which will be further called original, we will carry out the following imaginary experiment. Subdividing the time scale of the original to

sufficiently small time intervals, Δt_i ($i = 1, 2, \ldots, n$), we will perform n experiments starting from the beginning of each Δt_i.

Thus, we can determine n residual enthalpies, $\Delta H_{r,i}$. The first residual enthalpy difference $\Delta^R(\Delta H)_1 = (\Delta H_{r,0} - \Delta H_{r,1})$ should be equal to the first partial enthalpy release as measured from the original, $\Delta^O(\Delta H)_1$; the second residual enthalpy difference $\Delta^R(\Delta H)_2 = (\Delta H_{r,1} - \Delta H_{r,2})$ should be equal to the second partial enthalpy release $\Delta^O(\Delta H)_2$, etc., i.e.:

$$\Delta^R(\Delta H)_i = (\Delta H_{r,i-1} - \Delta H_{r,i}) = \Delta^O(\Delta H)_i \tag{A1}$$

where the superscripts "O" and "R" denote original and residual enthalpy data, respectively.

At the beginning we have $\Delta H_{r,0} = \Delta H_t$. From the point of view of the measuring analogy, the residual enthalpy corresponds to the remaining epoxy able to react, while the currently measured enthalpy represents the quantity of the product achieved.

The relationships between the molar and energy characteristics in an excess of amine can be obtained applying the QIAC measuring analogy starting from both the original and residual enthalpy data.

The product concentration as measured from the original must be equal to the epoxy and amine currently reacted fraction. It can be expressed as:

$$x = e_0 - e = a_0 - a = \frac{1}{\Delta H^0} \int_0^{t_n} \frac{d(\Delta H)}{dt}\, dt = \frac{\Delta H}{\Delta H^0} \tag{A2}$$

The initial and current epoxy and amine component concentrations are, respectively:

$$e_0 = \frac{\Delta H_t}{\Delta H^0} \quad \text{and} \quad a_0 = \frac{\Delta H_t R_a}{\Delta H^0} \tag{A3}$$

$$e = \frac{\Delta H_t - \Delta H}{\Delta H^0} \quad \text{and} \quad a = R\frac{\Delta H_t - \Delta H}{\Delta H^0} = \frac{\Delta H_t R_a - \Delta H}{\Delta H^0} \tag{A4}$$

Then, the current value of the amine to epoxy ratio becomes:

$$R = \frac{\Delta H_t R_a - \Delta H}{\Delta H_t - \Delta H} \tag{A5}$$

Now, let us consider the rate of reaction. The product concentration increase $(\Delta x)_1$ can be determined from the original data as $\Delta^O(\Delta H)_1$. At the same time, the partial decrease of epoxy concentration during the first time interval, $(\Delta e)_1$, can be determined from the first residual enthalpy difference, $\Delta^R(\Delta H)_1$.

Having in mind the equality of two enthalpy quantities described with the aid of Eq. (A1), the corresponding concentrations must be equal since they obey identical equations, viz.

$$(\Delta x)_1 = -(\Delta e)_1 = \frac{\Delta(\Delta H)_1}{\Delta H^0} \text{ in mol kg}^{-1}$$

Dividing by Δt_1, the rate of reaction must be proportional to the partial derivative, viz.

$$\left(\frac{\Delta x}{\Delta t}\right)_1 = -\left(\frac{\Delta e}{\Delta t}\right)_1 = \frac{\Delta(\Delta H)_1}{\Delta H^0 \Delta t} \text{ in mol kg}^{-1}\text{ s}^{-1}$$

The minus sign in the above equations means that e decreases whereas x increases. During the 2-nd, 3-th, and n-th time interval, Δt_n, the QIAC instrument will measure:

$$(\Delta x)_2 = -(\Delta e)_2 = \frac{\Delta(\Delta H)_2}{\Delta H^0}, \quad \text{and} \quad (\Delta x)_n = -(\Delta e)_n = \frac{\Delta(\Delta H)_n}{\Delta H^0}$$

and dividing by Δt:

$$\left(\frac{\Delta x}{\Delta t}\right)_2 = -\left(\frac{\Delta e}{\Delta t}\right)_2 = \frac{\Delta(\Delta H)_2}{H^0 \Delta t},$$

$$\text{and} \ldots \left(\frac{\Delta x}{\Delta t}\right)_n = -\left(\frac{\Delta e}{\Delta t}\right)_n = \frac{\Delta(\Delta H)_n}{H^0 \Delta t}$$

Hence, $(\Delta x)_i$ can be derived from $\Delta^O(\Delta H)_i$ of the original, while $(\Delta e)_i$ can be determined from the i-th residual enthalpy difference, $\Delta^R(\Delta H)_i$. Since the DSC signal is obtainable at $\Delta t \to 0$, $d(\Delta H)/dt$ will be linearly proportional to the rate of consumption of minority (epoxy) component or to the rate of reaction in the product equation, viz.

$$\frac{dx}{dt} = -\frac{de}{dt} = \frac{d(\Delta H)}{\Delta H^0 \, dt} \tag{A6}$$

Having in mind the equivalence between Eqs. (A6) and (6) in the main text, it can be concluded that the epoxy concentration/enthalpy release analogy works. These quantities can be converted from each other considering both QIAC and DSC experiments carried out in an excess of amine.

Appendix B. Analysis of the reaction rate definition in an excess of epoxy

The relationships between molar and enthalpy characteristics in an excess of epoxy are also based on Eq. (A2). According to Eq. (A2), the initial and current concentrations of epoxy and amine component can be expressed as [5–9]:

$$e_0 = \frac{\Delta H_t}{R_a \Delta H^0} \quad \text{and} \quad a_0 = \frac{\Delta H_t}{\Delta H^0} \tag{A7}$$

$$e = \frac{\Delta H_t - \Delta H}{R \Delta H^0} = \frac{\Delta H_t/R_a - \Delta H}{\Delta H^0} \quad \text{and} \quad a = \frac{\Delta H_t - \Delta H}{\Delta H^0} \tag{A8}$$

In agreement, the current value of the amine to epoxy ratio in an epoxy excess system is supposed to obey the equation [8]:

$$R = \frac{\Delta H_t - \Delta H}{\Delta H_t/R_a - \Delta H} \tag{A9}$$

We will try to prove that the classical definition of reaction rate based on the assumption that the heat flow signal is linearly proportional to the rate of consumption of the minority (amine) component is not correct in an excess of epoxy, although there must be the equality:

$$\frac{d(\Delta H_t - \Delta H)}{dt} = \frac{d[(\Delta H_t - \Delta H/R)]}{dt} \tag{A10}$$

However, the corresponding integral quantities $(\Delta H_t - \Delta H)/R_a$ and $(\Delta H_t - \Delta H)/R$ differ at any time by R_a/R, i.e. the time scales of both derivatives are not same. Then, the question is what derivative is being monitored applying DSC to epoxy excess systems.

Considering the commented imaginary experiment, the situation in an excess of epoxy is different. The current epoxy concentration can be determined from the residual enthalpy data following the equation:

$$e_i = \frac{\Delta H_{r,i}}{R_i \Delta H^0} \tag{A11}$$

where e_i and R_i are the initial values of epoxy concentration and amine to epoxy ratio derived from each residual enthalpy data curve.

The original data set which can be treated as zero residual enthalpy data yields:

$$e_0 = \frac{\Delta H_t}{R_a \Delta H^0} \tag{A12}$$

Dividing Eq. (A11) by Eq. (A12), one can obtain the normalized relationship:

$$\frac{e_i}{e_0} = \frac{R_a}{R_i} \frac{\Delta H_{r,i}}{\Delta H_t} \tag{A13}$$

The last equation can be rearranged into the form:

$$1 - \frac{e_i}{e_0} = \frac{e_0 - e_i}{e_0} = 1 - \frac{R_a}{R_i} \frac{\Delta H_{r,i}}{\Delta H_t} \tag{A14}$$

The enthalpy which can be measured from the original within $t = t_i$ and $t = t_n$, i.e. $\Delta H_i = \Delta H_t - \Delta H$, has to be equal to the corresponding residual enthalpy data, viz. $\Delta H_i = \Delta H_{r,i}$. It can be expressed by a rearrangement of Eq. (A2) as:

$$e_0 - e = \frac{1}{\Delta H^0} \int_0^{t_i} \frac{d(\Delta H)}{dt} dt$$

$$= \frac{1}{\Delta H^0} \left(\int_0^{t_n} \frac{d(\Delta H)}{dt} dt - \int_{t_i}^{t_n} \frac{d(\Delta H)}{dt} dt \right) = \frac{\Delta H_t - \Delta H_i}{\Delta H^0} \tag{A15}$$

Then, using the original one can measure the totally converted epoxy quantity, viz.

$$(e_0 - e_f) = \frac{\Delta H_t}{\Delta H^0} \tag{A16}$$

Dividing Eq. (A15) by Eq. (A16), it can be defined the following normalized variable in respect to the excess (epoxy) component:

$$\alpha = \frac{e_0 - e}{e_0 - e_f} = \left(1 - \frac{e}{e_0}\right) \frac{1}{R_a} = 1 - \frac{\Delta H_i}{\Delta H_t} = 1 - \alpha' \tag{A17}$$

One can accept another representation of Eq. (A17), viz.

$$\beta = \frac{a_0 - a}{a_0} = 1 - \frac{a}{a_0} = 1 - \frac{\Delta H_i}{\Delta H_t} = 1 - \lambda \tag{A18}$$

The last equation is based on the assumption that the minority component variable β must be formally identical with the excess (epoxy) component variable α [5–8]. At the same time, the relationship between the measurements λ and α' must be a function of R/R_a, in agreement with Eq. (A14). Note that $\Delta H_i = \Delta H_{r,i}$ by definition, although the measurement ΔH_i obtained from the original is time dependent while the residual enthalpy measurement $\Delta H_{i,r}$ is not.

We will consider below the reaction rate from the point of view of both QIAC and DSC experiments. Following the above presented imaginary experiment, the first residual enthalpy difference yields the quantity with respect to the epoxy, viz.

$-(\Delta e)_{r,1} = \Delta^R(\Delta H)_1/(R_a \Delta H^0)$ in mol kg^{-1} (epoxy); and $-\left(\Delta e/\Delta t\right)_{r,1} = \Delta^R(\Delta H)_1/(R_a \Delta H^0 \Delta t)$ in mol kg^{-1} s^{-1}.

At the same time, Eq. (A2) predicts the concentration change with respect to the product:$(\Delta x)_1 = \Delta^O(\Delta H)_1/(R_a \Delta H^0)$ in mol kg^{-1} (product); and $(\Delta x/\Delta t)_1 = \Delta^O(\Delta H)_1/(R_a \Delta H^0 \Delta t)$ in mol kg^{-1} s^{-1} and the quantities calculated with respect to the epoxy, viz.$-(\Delta e)_1 = \Delta^O(\Delta H)_1/(R_a \Delta H^0)$ in mol kg^{-1} (product); and $-(\Delta e/\Delta t)_1 = \Delta^O(\Delta H)_1/(R_a \Delta H^0 \Delta t)$ in mol kg^{-1} s^{-1}.

The equations derived on the basis of the trivial renormalization of the original will be neary valid only within the 1-st time interval. At the end of the 2-nd time interval, Δt_2, it can be obtained from the second residual enthalpy difference the following quantity:

$$-(\Delta e)_{r,2} = \frac{\Delta^R(\Delta H)_2}{R_1 \Delta H^0} \quad \text{and} - \left(\frac{\Delta e}{\Delta t}\right)_{r,2} = \frac{\Delta^R(\Delta H)_2}{R_1 \Delta H^0 \Delta t}$$

since the molar amine to epoxy ratio has changed from $R_0 = R_a$ to R_1 according to Eq. (A4), i.e. there must be accounted the enthalpy release up to the beginning of this time interval.

On the other hand, the corresponding product and epoxy quantities as determined from the original must obey by definition

different equations, viz.

$$(\Delta x)_2 = -(\Delta e)_2 = \frac{\Delta^O(\Delta H)_2}{R_a \Delta H^0}$$

$$\text{and} \quad \left(\frac{\Delta x}{\Delta t}\right)_2 = -\left(\frac{\Delta e}{\Delta t}\right)_2 = \frac{\Delta^O(\Delta H)_2}{R_a \Delta H^0 \Delta t}$$

Transferring at the i-th time interval, Δt_i, it can be derived:

$$-(\Delta e)_{r,i} = \frac{\Delta^R(\Delta H)_i}{R \Delta H^0} \quad \text{and} \quad -\left(\frac{\Delta e}{\Delta t}\right)_{r,i} = \frac{\Delta^R(\Delta H)_i}{R \Delta H^0 \Delta t} \tag{A20}$$

from the residual enthalpy data, and:

$$(\Delta x)_i = -(\Delta e)_i = \frac{\Delta^O(\Delta H)_i}{R_a \Delta H^0}$$

$$\text{and} \quad \left(\frac{\Delta x}{\Delta t}\right)_i = -\left(\frac{\Delta e}{\Delta t}\right)_i = \frac{\Delta^O(\Delta H)_i}{R_a \Delta H^0 \Delta t} \tag{A21}$$

from the original, respectively.

The comparison of Eqs. (A14) and (A18) shows that the two sets of integral data differ by R/R_a and the residual enthalpy data only reflect the epoxy concentration/enthalpy release analogy. The same conclusion can be drawn comparing two partial differences according to Eqs. (A20) and (A21), respectively. They can be correlated, as it follows:

$$\frac{\Delta x}{\Delta t} \propto -\frac{\Delta e}{\Delta t} = \frac{\Delta(\Delta H)}{\Delta H^0 \Delta t} \tag{A22}$$

The last equation implies that the time scale of the original QIAC experiment is not the scale of the normalized minority component profile. To obtain the reaction rate performing numerical differentiation, the profile $\Delta H/\Delta H^0$ of the original must be renormalized into $\Delta x/a_0$. According to this equation, the time scale shift must be a function of the ratio R/R_a.

Considering the difference between the original and residual enthalpy data obtained using real DSC equipment, it can be concluded that the linear definition of reaction rate through the heat flow signal does not hold, i.e. the DSC instrument does not differentiates the product (and minority component) quantity.

In agreement with the analysis performed in Section 2.1, it follows that:

$$\frac{d(x/a_0)/dt}{[-d(e/e_0)/dt]} = \frac{d(x/a_0)/dt}{d(\Delta H)/\Delta H_t dt} = \frac{R_a}{R} \tag{A23}$$

The only debatable point that remained unsolved is: what quantity is being measured applying DSC to epoxy excess systems if the epoxy concentration/enthalpy release analogy is supposed to be correct. The key of the problem consists in the "hidden normalization" of the DSC signal, thus measuring *the fraction of epoxy able to react*. In agreement with the fundamentals of the kinetics, the quantities in the rate equation in an absolute concentration form – where such problem does not exists – must be *the total concentration of epoxy (and its time derivative)* or a physical property measurement yielding linearly proportional values.

Following the fundamental derivative expression in the kinetics:

$$\frac{da}{dt} = \frac{de}{dt} = -\frac{dx}{dt} \tag{A24}$$

the reactant derivatives can be described with the aid of the model,

$$\frac{1}{f(a,e)ea} \frac{da}{dt} = \frac{1}{f(a,e)ea} \frac{de}{dt} \tag{A25}$$

where $F(a,e)$ in Eq. (A25) is the remaining part of the model function.

The last equation can be further rearranged, as it follows:

$$\frac{d[\ln(a)]}{dt} = \frac{e}{a} \frac{d[\ln(e)]}{dt} = \frac{1}{R} \frac{d[\ln(e)]}{dt} \tag{A26}$$

An identical rearrangement of the normalized derivatives yields the expression:

$$\frac{d[\ln(a_0/a)]}{dt} = \frac{R_a}{R}\frac{d[\ln(e/e_0)]}{dt} \tag{A27}$$

The corollaries reasoning from Eqs. (A23) and (A27) are commented in the main text.

Appendix C. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2008.08.012.

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