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THE KINETICS OF MODEL REACTIONS OF CURING EPOXY RESINS WITH AMINES

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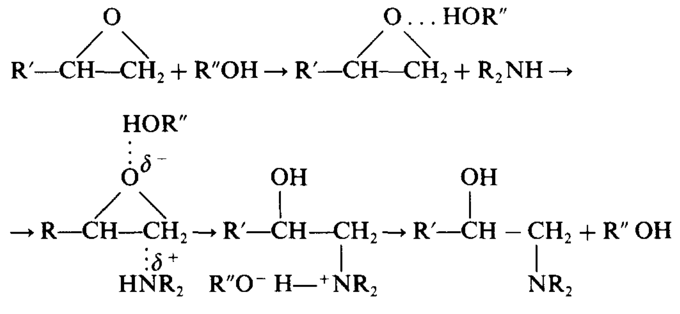
Abstract—The isothermal course of the reaction of phenylglycidyl ether and *N,N*-methylglycidylaniline with dibutyl amine at various temperatures was investigated DSC. The data were treated on the basis of a reaction scheme with two processes in parallel, one of them auto-catalyzed. A good fit with the experiment was reached only when the order of both processes with respect to amine had been reduced to half its original value. An assumption that the kinetics of the amine–epoxy resin rection are considerably affected by the formation of various complexes through hydrogen bonds may be an explanation. A simple mathematical model has been suggested to estimate this influence. Because of the relatively high heats of interaction for the formation of complexes, the dependence of the measured heat on the degree of conversion is not linear. The magnitude of the error caused by neglecting this fact in investigation of the kinetics by DSC has been estimated.

INTRODUCTION

Differential scanning calorimetry (DSC) is a method often used in the investigation of the course of chemical processes; it is also employed for the reaction between epoxy resins and amines. The importance of substitution of oligofunctional monomers with monofunctional model compounds in the investigation of the kinetics of curing consists in that, at higher degrees of transformation, no complications can be caused by an increase in viscosity and gelation.

The following mechanism has been suggested for the reaction between a monofunctional epoxy resin and a secondary amine [1]:



(I)

One can see that the reaction is catalyzed by hydroxy derivatives which in this case act as proton donors. Since the hydroxy group is also present in the reaction product, the reaction is accelerated also without added alcohol, and it is then autocatalytic.

Scheme (I) is described by a kinetic equation

$$-\,\mathrm{d}\,[\mathrm{E}]/\mathrm{d}t = (k_2^0\,[C^\circ] + k_2\,[\mathrm{C}])\,[\mathrm{E}]\,[\mathrm{A}] \qquad (1)$$

in which square brackets symbolize molar concentrations, A, E, C represent respectively the secondary amine, epoxy resin and reaction product, C° is alcohol which has been intentionally added to the reaction mixture, or which is present as an impurity.

In other papers [2, 3], an uncatalyzed reaction in parallel with the catalyzed process is also considered, and it is assumed that $[C^\circ] = 0$. The expression $k_2^0\,[C^\circ]$ in Eqn (1) should then be replaced by the rate constant of the uncatalyzed reaction, k_1. It is assumed [4] that amine acts catalytically, similarly to alcohol, and the reaction between the amine alone and the epoxy resin is therefore regarded as second-order with respect to amine.

However, even with monofunctional reactants, neither the original nor the modified Eqn (1) can adequately represent the experiment over the whole range of conversion. Various empirical modifications have therefore been suggested. For a case where the compounds were mixed in a stoichiometric ratio (thus, [E] = [A] for each t), some of them may be written in a general form

$$-\,\mathrm{d}\,[\mathrm{E}]/\mathrm{d}t = (k_1 + k_2\,[\mathrm{C}]^n)\,[\mathrm{E}]^m; \qquad (2)$$

the corresponding values for Eqn (1) are $n = 1$, $m = 2$. Ryan and Dutta [5] suggest that the sum of

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the exponents in Eqn (2) should be reduced to ($m + n = 2$), m and n being functions of temperature. Flammersheim [6] has modified the exponents in Eqn (2), so that $n = 1$, $m = 1.5$.

In the amine/epoxy resin reaction system, complex formation by means of hydrogen bonds can be regarded as proven, also at relatively high temperatures [7, 8]. These complexes may both accelerate the reaction (catalysis with proton-donor compounds) and retard it, due to the binding of some reactive groups. Arutjunjan [4] considers some of the likely complexes, e.g. A_1C, A_2C, A_3C and EC, where A_1, A_2, A_3 respectively denote the primary, secondary and tertiary amine.

This brief review of the literature shows that various approaches have been used to solve the problem of reaction kinetics between amine and the epoxy resin. We decided to use the simplest model systems (secondary amine/monofunctional epoxy resin) in order to verify the suitability of the DSC method for investigation of the reaction rate and to estimate the validity of some kinetic schemes. For this purpose, various values of the initial ratio of the amine and epoxy resin concentrations (β) were chosen, because the independence of the calculated rate constants on β is an important criterion of suitability of the kinetic model.

EXPERIMENTAL

Compounds

To investigate the kinetics of the amine/epoxy resin reaction, the following model compounds were used: phenylglycidyl ether—PGE (IMC CSAS, Prague; GC purity 99.53%), *N,N*-methylglycidylaniline—MGA 9 (99.34%) and dibutyl amine—DBA (Fluka AG, Buchs; 99.82%).

Measurements

The reaction was followed using a Perkin–Elmer DSC 2 calorimeter under isothermal conditions in the temperature range 373–433 K, according to the type of the reaction system used. The experiments have been described in greater detail [9].

TREATMENT OF EXPERIMENTAL DATA

Kinetic equations

The experiment was evaluated using four model schemes described by a common kinetic equation

$$-\mathrm{d}[\mathrm{E}]/\mathrm{d}t = k_1[\mathrm{E}][\mathrm{A}]^p + k_2[\mathrm{E}][\mathrm{A}]^q[\mathrm{C}]. \quad (3)$$

Tiltscher's concept [2] as described in the Introduction is satisfied by the exponents $p = 1$ and $q = 1$ in Eqn (3); this model is denoted as (i). Noting the previous conclusion [4] according to which the reaction is catalyzed either with amine or with a hydroxy derivative, we have introduced model (ii), for which $p = 2$ and $q = 1$. According to Flammersheim *et al.* [6], who worked exclusively at $\beta = 1$, the sum of the exponents for [E] and [A] should be reduced from 2 to 1.5. Our data for various β values have indicated that, in the case of model (i), the reaction order should be reduced with respect to amine, but not with respect to the epoxy resin. Let us therefore introduce model (iii), for which $p = q = 0.5$. If an analogous modification is carried out with model (ii), we obtain $p = 1$ and $q = 0.5$, i.e. model (iv). Exponents for the individual models are reviewed in Table 1. Let us define the degree of conversion as

$$\alpha = (n_\mathrm{E}^0 - n_\mathrm{E})/n_\mathrm{E}^0, \quad (4)$$

where n_E and n_E^0 are the amounts of substance of component E at a time t and $t = 0$.

If the initial ratio of the amounts of substance of reactants is

$$\beta = n_\mathrm{A}^0/n_\mathrm{E}^0 \quad (5)$$

and the ratio of their molar volumes is

$$\Phi = V_\mathrm{A}/V_\mathrm{E}, \quad (6)$$

then

$$\frac{1-\alpha}{[\mathrm{E}]} = \frac{\beta-\alpha}{[\mathrm{A}]} = \frac{\alpha}{[\mathrm{C}]} = \frac{V}{n_\mathrm{E}^0} = V_\mathrm{E}(1+\Phi\beta) \quad (7)$$

where V is the total volume of the system, and Eqn (3) can be rewritten as

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k_1\frac{(1-\alpha)(\beta-\alpha)^p}{[V_\mathrm{E}(1+\Phi\beta)]^p} + k_2\frac{(1-\alpha)(\beta-\alpha)^q\alpha}{[V_\mathrm{E}(1+\Phi\beta)]^{q+1}} \quad (8)$$

The equation thus formulated for the time dependence of degree of conversion allows us to check the independence of the constants k_1, k_2, evaluated from the data obtained, on the ratio of components β; this is made noting that the overall volume of the reaction system varies with β, also if n_E^0 is unity.

If we now define the auxiliary quantity

$$r_r = \frac{\mathrm{d}\alpha/\mathrm{d}t}{(1-\alpha)(\beta-\alpha)^p}[V_\mathrm{E}(1+\Phi\beta)]^{q+1}, \quad (9)$$

we obtain Eqn (8) in a linearized form

$$r_r = k_1[V_\mathrm{E}(1+\Phi\beta)]^{q-p+1} + k_2\alpha(\beta-\alpha)^{q-p}. \quad (10)$$

The slopes of the straight lines are equal to k_2; k_1 can be calculated from the intercept.

A model calculation of the reaction course affected by complex formation

As can be seen from some reported data [4, 10] and from our own results [9], an important role in the reaction between amine and the epoxy resin is played by the formation of various complexes through hydrogen bonds, also at relatively high reaction temperatures. However, DSC measurements do not provide data on the individual types of these complexes and their effect. We therefore suggest a simple mathematical model which would adequately describe their functioning. It is assumed that complexes may arise in the reaction mixture due to the formation of the following hydrogen bonds: AC, CC, EC, AA, where A is now related to the –NH– group of the secondary amine, E to the oxygen in the epoxy group, and C to the hydroxy group of the reaction product. The "strength" of these bonds decreases in the order

Table 1. Exponents of Eqn (3)

	Model			
	(i)	(ii)	(iii)	(iv)
p	1	2	0,5	1
q	1	1	0,5	0,5
$q-p$	0	−1	0	−0,5

from AC to AA. Furthermore, our model contains some simplifying assumptions:

—the individual association functionalities interact independently of the fact whether such functionality in the same molecule is already bound in the complex;

—all the functionalities in multifunctional molecules are equivalent. The actual concentrations of the individual reaction components and of the product can be expressed by using concentrations of free association functionalities f_A, f_E, f_C. The association functionality need not equal the reaction functionality. Here, with respect to association, the secondary amine and the alcohol are regarded as bifunctional and the epoxide, as monofunctional. Thus, the balance

$$2[A] = 2\frac{\beta - \alpha}{V_E(1 + \Phi\beta)} = f_A + \sigma_A f_A^2 + \eta_A f_A f_C \quad (11a)$$

$$[E] = \frac{1 - \alpha}{V_E(1 + \Phi\beta)} = f_E + \eta_E f_E f_C \quad (11b)$$

$$2[C] = 2\frac{\alpha}{V_E(1 + \Phi\beta)} = f_C + \eta_A f_A f_C + \eta_E f_E f_C + \sigma_C f_C^2 \quad (11c)$$

is valid, where η_A, η_E, σ_C, σ_A are the equilibrium constants of hydrogen bond formation.

By solving the system of Eqns (11), f_A, f_E, f_C may be calculated for various α at the chosen values of the ratio β and of the binding constants.

In expression (3) for the reaction rate we put $p = q = 1$, and $[K] = f_K$, where K is the reaction component.

Correction for heats of interaction

The use of calorimetric methods in the investigation of reaction kinetics is based on an assumption that the heat of reaction developed within the time from 0 to t is proportional to the degree of conversion α:

$$\alpha(t) = \frac{H(t) - H(0)}{H(\infty) - H(0)} . F(\beta) \quad (12)$$

where $H(t)$ is the enthalpy of the system at a time t. The equation holds, assuming that after a sufficiently long time the reaction proceeds quantitatively. The function $F(\beta)$ is defined in Appendix A; in Eqn (12) it has been used noting that α is related to the initial amount of the epoxy resin, while the fraction on the right-hand side of Eqn (12) is based on the amount of the minority component.

In the amine/epoxy resin reaction system, there are strong thermodynamic interactions between the components; the heats of interaction cannot be neglected with respect to the heats of reaction, and they are a non-linear function of the degree of conversion. Hence, into Eqn (12) we must substitute

$$H(t) = H_e(t) - H_i(t), \quad (13)$$

where $H_e(t)$ is the total enthalpy, $H_i(t)$ is the enthalpy of interaction, and $H(t)$ is now the sum of enthalpies of the pure components present at time t. Similarly, we substitute for $t = 0$ and $t = \infty$. Furthermore, introduced

$$\Delta H_e(t) = H_e(t) - H_e(0) \quad (14)$$

for the heat experimentally determined within the time t, since the beginning of the reaction. Below, the enthalpy and heats at complete conversion are denoted with an asterisk:

$$H_i^* \cong H_i(\infty) \quad (15)$$

$$\Delta H_e^* \cong H_e(\infty) - H_e(0) \quad (16)$$

The $H_i(t)$ dependence cannot be directly estimated from DSC measurements, but it is possible to estimate the dependence of H_i on α from theory. The only available source of data on the heats of interactions is the dependence of H_e on the ratio β of the initial concentrations (Fig. 1, Ref. [9]); by evaluating this dependence, two parameters at most can be obtained. This is why we estimated the $H_i(\alpha)$ dependence by using a simple Flory–Huggins model, assuming random mixing of the components A, E and C.

In Appendix B, we derive the equation

$$H_i(\alpha) = \frac{h_{AC}(\beta - \alpha)\alpha + h_{EC}(1 - \alpha)\alpha}{V_E(1 + \Phi\beta)F(\beta)} \quad (17)$$

The enthalpic interaction parameters h_{AC} and h_{EC} can be calculated from

$$h_{AC} = [\Delta H_e^*(\beta) - \Delta H_e^*(1)]\, V_E \times (1 + \Phi\beta)/(\beta - 1);\ \beta > 1 \quad (18a)$$

$$h_{EC} = [\Delta H_e^*(\beta) - \Delta H_e^*(1)]\, V_E \times (1 + \Phi\beta)/(1 - \beta);\ \beta < 1 \quad (18b)$$

From what has been said above, we have the following iteration procedure. By using Eqns (13)–(16) and Eqn (B8), Eqn (12) may be rearranged to

$$\alpha(t) = \frac{\Delta H_e(t) - H_i(t)}{\Delta H_e^* - H_i^*} F(\beta) \quad (19)$$

Here, we put in the first approximation $H_i(t) = 0$, $H_i^* = 0$. By combining the dependence $\alpha(t)$ thus obtained with Eqn (17), we obtain another approximation of $H_i(t)$, and the procedure is repeated by means of Eqns (B5a,b).

The model is only approximately correct, due to the random mixing assumed in deriving it. This is why h_{AC} and h_{EC} are not entirely independent of β. The h_{AC} value for $\beta = 2$ and the h_{EC} value for $\beta = 0.5$ were used in the calculation.

RESULTS AND DISCUSSION

Kinetics of the reaction amine/epoxy resin

Examples of linearized kinetic equations are given in Figs 1a–1d. Kinetic data obtained using model (i) for the reaction systems DBA/FGE and DBA/MGA (Fig. 1a and 1b) show that the dependence of reduced reaction rate (r_r) on α is linear for only a restricted range of α ($0 \leqslant \alpha \leqslant \alpha_1$), the upper boundary of which is a function of the initial molar ratio of the two components (β). The values of the rate constants k_2 (reaction between amine and the epoxy resin catalyzed with hydroxyls) are also a function of β. This finding may be explained by the fact that the hydroxy derivative arising during the reaction [scheme (I)] is bound in a complex with the still unreacted amine, and so loses its catalytic activity. Figures 1a and 1b also illustrate that MGA is less reactive than FGE; to

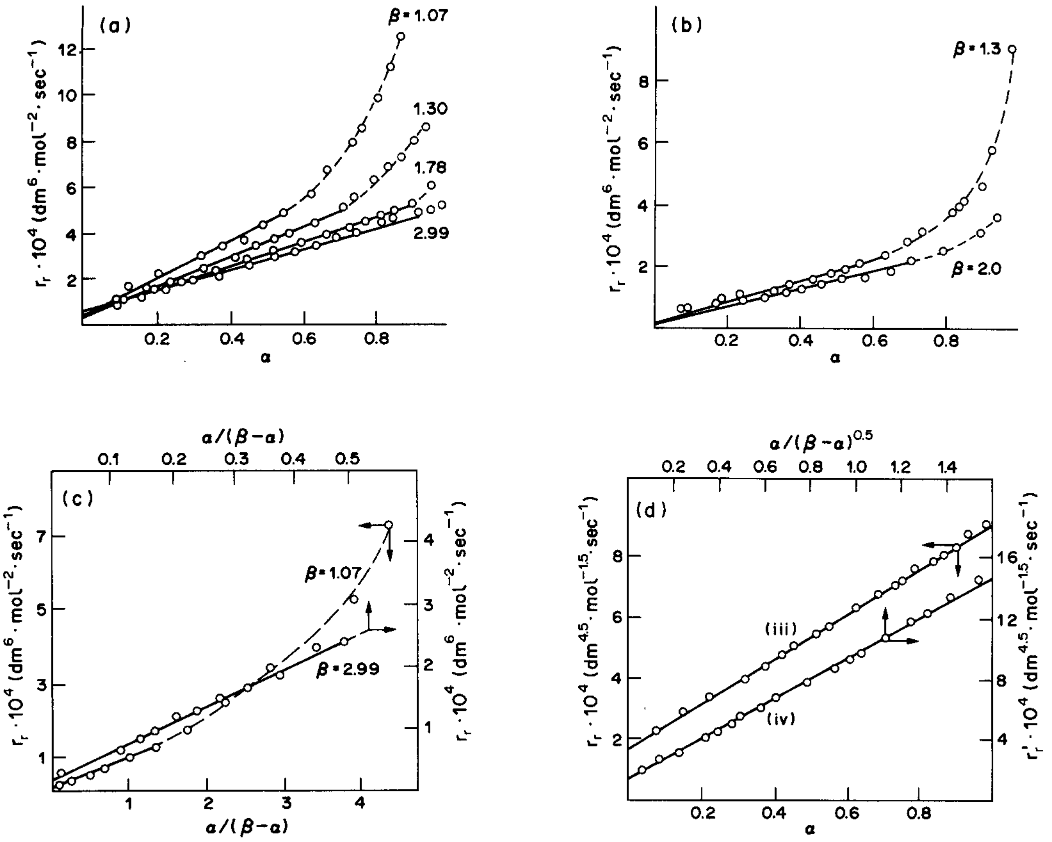

Fig. 1. A linearized plot of the reaction rate against the degree of transformation using Eqn (10). Solid lines correspond to the range of α values within which linear regression was performed ($\alpha < \alpha_l$, cf. Table 1). A broken line was plotted through the other points. (a) System DBA/FGE at 393.2 K, plot according to model (i) for the given β values. (b) System DBA/MGA at 423.2 K, plot according to model (i) for the given β values. (c) System DAB/FGE at 393.2 K, plot according to model (ii) for the given β values. (d) System DBA/FGE at 393.2 K, plot according to models (iii) and (iv) for $\beta = 1.3$.

make the k_1, k_2 values approximately the same as those of FGE, the temperature should be raised by some 40 K.

Evaluation of the kinetic parameters using model (ii) meets with difficulties similar to those for the first model (Fig. 1c). This is why our measurements do not allow us to decide which kinetic scheme better describes the reactions reported above, and whether the reaction between the amine and the epoxy resin without the participation of hydroxy groups can be described as second- or third-order.

The decrease of the reaction order with respect to amine according to models (iii) and (iv) has as the consequence that the r_r vs α, or $\alpha/(\beta-\alpha)^{0.5}$ plot is linear up to $\alpha = 0.9$ (Fig. 1d). Also the last two models satisfy the requirement of the independence of k_2 of β much better than the former two. This could best be illustrated using the DBA/FGE system at 383.2 K, when an optimized straight line with the slopes $10^4\,dk_2/d\beta$: (i) −0.89, (ii) −1.03, (iii) +0.12, (iv) −0,08 could be plotted through six data for various β values.

The k_1 values are more scattered than the k_2 values: Figs 1a–1d show that in the given case the parameter obtained from the intercept will be subject to larger error than that obtained from the slope. For this reason, we did not examine the models for the variation of k_1 with β.

Table 2 contains the values of the constants k_1, k_2 obtained by procedure (iii).

From the dependence of k_1, k_2 on temperature, the activation energies E_{A1} (reaction of amine alone with the epoxy resin) and E_{A2} (reaction catalyzed with hydroxyls) were determined. The average values are 70 kJ/mol for E_{A1} and 45 kJ/mol for E_{A2}. The higher values for E_{A1} suggest that the reaction between the amine and the epoxy resin with participation of –OH groups proceeds predominantly at lower temperatures; with increasing temperature, the participation of the reaction of amine alone with the epoxy resin increases. This finding is in agreement with earlier results [3].

The effect of complex formation on the reaction course

The DBA/FGE system at 393.2 K was chosen as the reference system for model calculations. First, by using reported data on analogous systems [12], we estimated the range in which the values of the binding constants (σ_A, σ_C, η_A, η_E) can be regarded as acceptable at the given temperature for the given types of hydrogen bonds. In this range we sought values which lead to an analogous dependence of the re-

Table 2. Kinetic parameters obtained using model (iii) by means of Eqn (10)

System	Temperature [K]	β	α_l†	$k_1\,10^4$/ (dm$^{1.5}$ mol$^{-0.5}$ sec^{-1})	$k_2\,10^4$/ (dm$^{4.5}$ mol$^{-1.5}$ sec^{-1})	R‡
DBA/FGE	373.2	1.45	0.907	1.58	3.06	0.9905
		2.20	0.901	1.40	3.00	0.9971
	383.2	1.14	0.908	3.05	4.80	0.9991
		1.20	0.906	2.95	5.08	0.9997
		1.45	0.908	2.86	4.72	0.9998
		1.92	0.904	2.36	5.04	0.9990
		2.18	0.907	1.98	4.99	0.9974
		2.92	0.906	1.76	5.08	0.9926
	393.2	1.07	0.880	4.48	9.79	0.9793
		1.30	0.900	4.71	7.30	0.9997
		1.78	0.912	4.06	6.55	0.9994
		2.18	0.883	4.35	7.22	0.9959
		2.99	0.978	2.40	8.02	0.9897
DBA/MGA	423.2	1.14	0.816	4.98	4.88	0.9256
		1.30	0.800	2.03	3.92	0.9920
		1.41	0.874	1.82	3.72	0.9947
		2.00	0.845	1.52	3.90	0.9924
	433.2	1.41	0.853	2.46	5.42	0.9920
		1.60	0.817	3.69	4.15	0.9966
		2.93	0.866	2.45	6.06	0.9812

†Upper boundary of linear dependence. ‡Correlation coefficient.

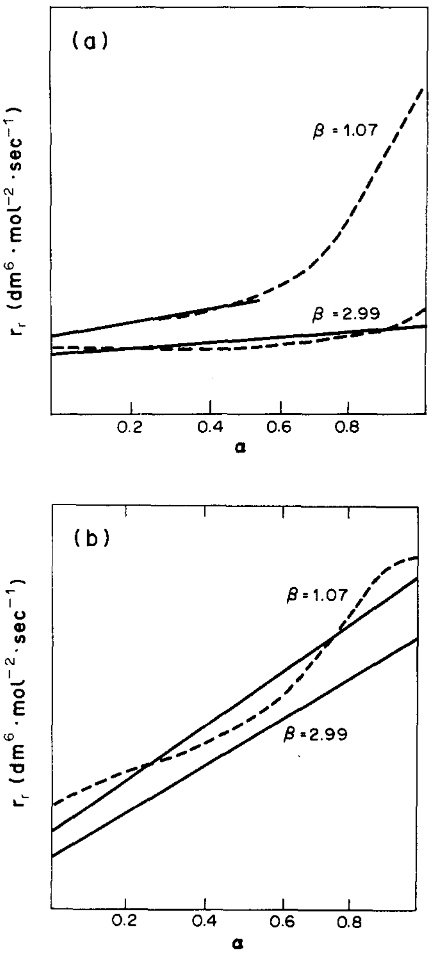

Fig. 2. Effect of formation of hydrogen-bond complexes on the reaction course. Reaction rate calculated from the theoretical model according to Eqn (11) and linearized according to scheme (i) (Fig. 2a) and (iii) (Fig. 2b). Meaning of solid and broken lines, as in Fig. 1.

Table 3. Comparison between k_1 and k_2 values calculated using scheme (iii) before and after correction for heats of interaction (system DBA/FGE; 393.2 K)

	$k_1\,10^4$/(dm$^{1.5}$ mol$^{-0.5}$ sec^{-1})		$k_2\,10^4$/(dm$^{4.5}$ mol$^{-1.5}$ sec^{-1})	
β	Uncorrected	Corrected	Uncorrected	Corrected
1.07	4.48	4.62	9.79	9.71
2.99	2.40	2.55	8.02	8.08

duced reaction rate (r_r) on α and to the same ratio of the rate constants k_2 for two boundary β values as in the experiment.

If the model calculation was carried out as already described, i.e. the expression for the reaction rate [Eqn (3)] comprised only the concentrations of free groups, f_A, f_E, f_C, the model did not fit the experiment. Instead of a pronounced acceleration of the reaction at higher conversions and at β approaching unity, the model course of r_r was quite different. When, on the other hand, the concentration of free amine groups f_A was replaced in the calculation by the total amine concentration [A], a comparatively good fit with the experiment was reached, as shown by comparison between Fig. 2 and Figs 1a to 1d. This seems to suggest that both the free and the complex-bound amine take part in the reaction. This hypothesis has already been substantiated [11]. The experiment is best described by a model having the following values of the binding constants: $\sigma_A = 0.04$ dm^3 mol^{-1}, $\sigma_C = 4$ dm^3 mol^{-1}, $\eta_A = 4.8$ dm^3 mol^{-1} and $\eta_E = 0.3$ dm^3 mol^{-1}.

Corrections for the heats of interaction

The effect of the heats of interaction was taken into account by using Eqns (17), (19) and (B5). From Table 3 we have that the heats of interaction, though considerable in the amine–epoxy resin reaction system [9], have an almost negligible influence on the eventual values of the calculated rate constants.

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APPENDIX A

Heat Effect Related to the Minor Component

If the ratio of the starting concentrations of reacting components β is not unity, it is the starting amount of the minor component that fixes the maximal amount of the major component able to react. To make the heat of reaction in complete conversion (in the absence of side reactions and of the heat due to the thermodynamic interaction) independent of β, it must be related to the unit amount of the minority component. The relation between the heat ΔH thus defined and the heat $\Delta H'$ related to the unity amount of the epoxy resin is given by

$$\Delta H' = \Delta H\, F(\beta), \tag{A1}$$

where

$$\begin{aligned} F(\beta) &= \beta \quad \beta \leqslant 1 \\ F(\beta) &= 1 \quad \beta \geqslant 1 \end{aligned} \tag{A2}$$

because the epoxy resin is the minor component for $\beta > 1$.

APPENDIX B

Dependence of the Heat of Interaction on the Degree of Transformation Reaction

According to the Flory–Huggins model, the enthalpy of mixing of a ternary system A/E/C is given by

$$H_{\mathrm{M}} = \kappa_{\mathrm{AE}} n_{\mathrm{A}} \phi_{\mathrm{E}} + \kappa_{\mathrm{AC}} n_{\mathrm{A}} \phi_{\mathrm{C}} + \kappa_{\mathrm{EC}} n_{\mathrm{E}} \phi_{\mathrm{C}} \tag{B1}$$

where ϕ_K is the volume fraction of component K and κ_{KL} is the enthalpic part of the interaction parameter between components K and L. The heat of interaction related to one mole of the minor component is

$$H_i = H_M / [n_E^0 F(\beta)] \tag{B2}$$

By using relations $n_K = V[K]$ and $\phi_K = V_K[K]$ and by substituting from Eqn (7), we obtain

$$H_i(\alpha) = \frac{h_{\mathrm{AE}}(\beta - \alpha)(1 - \alpha) + h_{\mathrm{AC}}(\beta - \alpha)\alpha + h_{\mathrm{EC}}(1 - \alpha)\alpha}{V_{\mathrm{E}}(1 + \Phi\beta)\, F(\beta)} \tag{B3}$$

where $h_{\mathrm{KL}} = V_{\mathrm{L}} \kappa_{\mathrm{KL}}$.

For $t \to \infty$ we have

$$\alpha = F(\beta) \tag{B4}$$

whence

$$H_i^*(\beta) = h_{\mathrm{AC}} \frac{\beta - 1}{V_{\mathrm{E}}(1 + \Phi\beta)} \quad \text{for} \quad \beta \geqslant 1 \tag{B5a}$$

$$H_i^*(\beta) = h_{\mathrm{EC}} \frac{1 - \beta}{V_{\mathrm{E}}(1 + \Phi\beta)} \quad \text{for} \quad \beta \leqslant 1 \tag{B5b}$$

For $\beta = 1$ we have

$$H_i^*(1) = 0 \tag{B6}$$

because the completely reacted system then contains only the pure component C.

For $t = 0$ we have $\alpha = 0$, and thus

$$H_i(0) = h_{\mathrm{AE}} \frac{\beta / F(\beta)}{V_{\mathrm{E}}(1 + \Phi\beta)} \tag{B7}$$

From data on the heats of mixing of amines, ethers and alcohols [12], it may be assumed that $|h_{\mathrm{AE}}| \ll |h_{\mathrm{EC}}| < |h_{\mathrm{AC}}|$; therefore put $h_{\mathrm{AE}} = 0$, and we obtain

$$H_i(0) = 0 \tag{B8}$$

From Eqn (B2) we have, then

$$\Delta H^* = \Delta H_e^*(\beta) - \Delta H_i^*(\beta) \tag{B9}$$

On the left-hand side of Eqn (B9) we have the pure reaction heat for $t \to \infty$, which is not a function of β (cf. Appendix A). Hence, by using relation (B6), we have

$$H_i^*(\beta) = \Delta H_e^*(\beta) - \Delta H_e^*(1) \tag{B10}$$

If we use this relation for substitution into Eqns (B5a,b), we obtain Eqns (18) for the calculation of the parameters h_{AC}, h_{EC}, using the dependence of the measured heat of reaction ΔH_e^* on β.