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Has the Elimination of Water to be Taken into Account in Polyesterification Kinetics?

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Summary

Various kinetic calculation methods taking the elimination of water into consideration or not, are reviewed and commented.

It is necessary to distinguish clearly the cases where the balance of reactants is stoichiometric and the cases where it is not.

It is shown that in the case where the balance is stoichiometric, no correction is needed as long as concentrations and not extents of reaction are used in equations.

When the balance of reactants is non stoichiometric a correction is necessary. The modified equations are given.

Introduction

During the course of a polyesterification the volume and the weight of the reaction mixture are modified because the condensation water is released. In most cases the titration of acid groups at determined times is used to follow the progress of the reaction ; the carboxyl group concentration is

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expressed in equivalents per kilogram. In consequence several authors tried to find out if the weight decrease due to the elimination of water must be taken into account.

Flory (1939) did no take into account this loss of weight as long as the extent of reaction p was not too low, without giving justification for this asumption. ($p = \frac{N_0 - N}{N_0}$ (1) where N_0 and N are the number of moles of carboxyl groups at times 0 and t respectively).

Most authors used this approximation with no further justification and moreover by using P (apparent extent of reaction) instead of p :

$$P = \frac{C_0 - C}{C_0} \quad (2)$$

(C_0 and C are the concentrations in carboxyl groups at times 0 and t respectively; they are determined experimentally).

However Szabo-Rethy (1971) showed that Flory's asumption leads to wrong values of rate constants and that the resulting error can be as high as 15 to 35%. This author gave a method of calculation which takes the elimination of water into consideration. Similar relations were used recently by Lin and Hsieh (1977) but in our opinion erroneously.

To restate the question in the present work we summarize the various methods of calculation which are reported in literature, we show that when the reaction is stoichiometric no correction is needed and we propose new relations for cases where the balance of reactive groups is non stoichiometric.

The general kinetic equation - case of stoichiometry

Since [COOH] = [OH] at any time the general kinetic equation (3) which is used by all authors :

$$- \frac{d\,[COOH]}{dt} = k\,[COOH]^m\,[OH]^n \qquad (3)$$

becomes

$$-\frac{dC}{dt} = k_d \quad C^d \qquad (4)$$

where d, m and n are the overall order and the orders relative to acid and alcohol respectively ($d = m + n$), k_d is the rate constant corresponding to a d overall order, and $C = [COOH]$ in eq. kg^{-1} at time t.

After integration (4) becomes (5) :

$$\begin{cases} \frac{1}{d-1}\left(\frac{1}{C^{d-1}} - \frac{1}{C_o{}^{d-1}}\right) = k_d t & d \neq 1 \\ \ln C_o/C = k_1 t & d = 1 \end{cases} \qquad (5)$$

where $C_o = [COOH]$ at initial time.

At any time t, $[COOH] = C$ and the reaction rate is $k_d C^d$, C being determined by titration. In consequence, the use of (5) requires no correction of the concentration.

A correction is needed however if parameters relative to the number of moles of reactants are introduced (e. g. p, or $\overline{DPn}$-degree of polymerization).

Let m_o and m be the weight of the reaction mixture at times 0 and t respectively and m_{H_2O} the weight of water released at time t.

Since $N_o = C_o.m_o$ (6) and $N = C.m$ (7) the relations :

$$\begin{cases} m_{H_2O} = 0.018\ (N_o - N) & (8) \\ m = m_o - m_{H_2O} & (9) \end{cases}$$

can be written :

$$\begin{cases} m_{H_2O} = 0.018\ (C_o.m_o - C.m) & (10) \\ m = m_o - 0.018\ (C_o.m_o - C.m) & (11) \end{cases}$$

thus

$$m = m_o \frac{1 - 0.018\ C_o}{1 - 0.018\ C} \qquad (12)$$

from (7) and (12) relation (13) can be obtained :

$$N = C \frac{1 - 0.018\ C_o}{1 - 0.018\ C} \cdot m_o \qquad (13)$$

and from (1) :

$$p = \frac{C_o - C\,\dfrac{1 - 0.018\,C_o}{1 - 0.018\,C}}{C_o} \tag{14}$$

Comparison of the relations (2) and (14) shows that a "corrected" concentration C^* must be used in place of C with :

$$C^* = C\,\frac{1 - 0.018\,C_o}{1 - 0.018\,C} \tag{15}$$

Flory's statement

The fundamental principle of Flory's statement (Flory, 1939) is relation (4). The data reported in Flory (1939) are relative to p, for the determination of which the corrections required to take into account the release of water have been carried out implicitely.

$$\overline{DP}_n = \frac{1}{1-p} = \frac{\overline{M}_n - 18}{\text{Mean segment weight}} \tag{16}$$

or

$$\frac{1}{1-p} = \frac{\overline{M}_n - 18}{\dfrac{M_A + M_B}{2} - 18} \tag{17}$$

where M_A and M_B are the molecular weights of diacid and diol monomers respectively.

Since $\frac{1}{C} = \frac{\overline{M}_n}{1000}$ (18), the experimental determination of C using equation (17) gives $\overline{DP}_n$ and p. This calculation differs slightly from those which have been established in the first part of this article but the results are the same :

Since

$$\frac{1}{C_o} = \frac{M_A + M_B}{2 \times 1000} \tag{19}$$

relation (17) becomes :

$$\frac{1}{1-p} = \frac{\dfrac{1}{C} - 0.018}{\dfrac{1}{C_o} - 0.018} \tag{20}$$

and relation (14) can be obtained from (20).

Although Flory takes into account the release of water in the determination of p, he does not do so in the following calculations assuming that :

$$p \approx P \quad (21) \quad \text{or} \quad C \approx C_o.(1-p) \quad (22)$$

which leads to :

$$dp/dt = k_d C_o^{d-1} \, . \, (1-p)^d \qquad (23)$$

Rate constants have been obtained by Flory (1939) from relation (23).

Corrected equation by Szabo-Rethy (1971)

If water elimination is taken into consideration in the determination of p it must also be taken into consideration throughout the calculation. In consequence relation (14) leads to :

$$C_o/C = (1-0.018\ C_o)\ \frac{1}{1-p} + 0.018\ C_o \qquad (24)$$

and from (2) :

$$\frac{1}{1-P} = (1-0.018\ C_o)\ \frac{1}{1-p} + 0.018\ C_o \qquad (25)$$

then
$$P = p\ \frac{1-0.018\ C_o}{1-0.018\ C_o.p} \qquad (26)$$

From (4) an equation similar to equation (23) can be obtained but it is necessary to replace p by P :

$$\left\{ \begin{array}{l} -\dfrac{dC}{dt} = k_d C^d \\ \\ \dfrac{1}{1-P} = \dfrac{C_o}{C} \end{array} \right. \Longrightarrow \frac{dP}{dt} = k_d\ C_o^{d-1}(1-P)^d \quad (27)$$

Corrected relation (27) is the true kinetic relation giving right values of k_d when used with P (apparent extent of reaction) but wrong values when used with p (exact extent of reaction). When p is used instead of P appreciable errors can occur ; these are analyzed by Szabo-Rethy (1971).

Other approximations

In several works published after Flory (e.g. Tang and Yao (1959)) water release is not taken into account either in the calculation of the extent of reaction or in the general kinetic relation. However these two approximations cancel each other and the final relation is correct.

Erroneous use of corrections

Lin and Hsieh (1977) take into consideration the removal of water and obtain relation (28) rewritten with our notations :

$$C^{*} = \frac{C(W_o - 18)\times 1000}{W_o(1000 - 18\ C)} \qquad (28)$$

where W_o is the total weight of the reaction mixture corresponding to one equivalent of diacid.

Relation (28) and our relation (15) are obviously the same. From relations (2) and (28) Lin and Hsieh (1977) obtain values of the extent of reaction, p. However they did not proceed to the necessary further corrections in (23).

It it obvious that the use of values of p (exact extent of reaction) in relation (23) is a source of error, in the same way as the use of corrected values of concentration, C^{*}, in relation (4).

Case of a non stoichiometric balance of the reactants

It seems that this case has never been examined. If only one reactant (e.g. acid) is titrated it results in :

$$[OH] = [COOH] + b_o \qquad (29)$$

where b_o is the algebraic excess of hydroxyl group concentration before the begining of the reaction. Relation (3) becomes : $- \frac{dC}{dt} = k_d \; C^m \; (C + b_o)^n$ (30)

When water is released the weight of the reaction medium decreases, and the true excess of the hydroxyl group concentration increases since the number of hydroxyl groups in excess does not change :

$$b_o \, . \, m_o = b \, . \, m \qquad (31)$$

where b is the excess of hydroxyl group concentration at time t.

Use of (12) leads to $b = b_o \frac{1 - 0.018 \; C}{1 - 0.010 \; C_o}$ (32)

which gives the following rate equation (33) :

$$- \frac{dc}{dt} = k_d C^m \; (C + b_o \; \frac{1 - 0.018 \; C}{1 - 0.018 \; C_o})^n \qquad (33)$$

It is obvious that if the two reactants are titrated independently equation (3) must be used without any correction.

CONCLUSION

As long as concentrations are used no correction is needed for stoichiometric reaction. When the balance is non stoichiometric, corrections must be carried out.

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