

Should the removal of water be taken into account in the analysis of kinetic data of polyesterification reactions?

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SUMMARY

In most polyesterification reactions, the concentrations of acid, alcohol and catalyst (if present) are expressed in moles per unit mass of the charge, denoted as moles/kg. In this paper, a general kinetic equation that takes water removal into account has been derived. It has been shown that (i) when the progress of reaction is followed by titration of acid, the removal of water affects the concentrations of alcohol and catalyst; and (ii) the ratio of the rate constants that do and do not account for water removal is smaller than unity, and it varies with the degree of reaction. On the other hand, it has been found that the rate constant obtained using moles/kg as the unit of concentration is not a real constant but a function of the charge density. Treating it as a constant may lead to appreciable error or misinterpretation.

INTRODUCTION

In most polyesterification reactions, it is common practice to express the concentrations of acid, alcohol and catalyst (if present) in moles per unit mass of the charge, denoted as moles/kg. As a result, their concentrations can be affected by the removal of the generated water molecules. Interestingly, in the literature, there exists the long-debated question of whether or not the removal of water should generally be taken into account in kinetic data treatment. Flory (1) was probably the first who developed a kinetic equation for polyesterification reactions, and he neglected the removal of water in his kinetic data treatment. Although his method has been used by most authors, it was subject to modifications (2, 3). Szabo-Rethy (4) showed that rate constants calculated by Flory's method could result in an error of 15% to 35%, and that it is not a real constant but a function of the degree of reaction. Marechal (5) derived a general kinetic equation that takes water removal into consideration. He concluded that if the concentration of acid is followed by titration and the reaction is stoichiometrically balanced, no correction is needed when concentrations instead of extents of reaction are used in kinetic equations; if the reaction balance is non-stoichiometric, the concentration of alcohol needs to be corrected. He also pointed out that some of the corrections in the literature are not appropriate. But his general equation, along with his conclusions, is pertinent only to specific cases. On the other hand, it is interesting that in the literature, the unit, moles/kg, has been widely used for the concentration without any fundamental justification.

The aim of this paper is therefore two-fold: (i) to develop a general kinetic equation that takes water removal into account while adopting the unit of moles/kg; and (ii) to gain insight into the relation between the rate constants using units of moles/kg and moles/l.

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FORMULATION OF A GENERAL KINETIC EQUATION

Starting with the following general kinetic equation, Marechal showed how to take water removal into account in polyesterification reactions:

$$-\frac{d[\text{COOH}]}{dt} = k[\text{COOH}]^m[\text{OH}]^n \quad (1)$$

where m and n are the reaction orders with regard to the concentrations (moles/kg) of acid and alcohol, respectively.

This is a general equation only when no external catalysts are present or overall reaction rates are independent of catalyst concentration. Thus his conclusions are correct only for these cases, even though he did not explicitly state so. The real general kinetic equation should also include the concentration of catalyst, and it can be of the following form:

$$-\frac{d[\text{COOH}]}{dt} = k[\text{Cat}]^x[\text{COOH}]^m[\text{OH}]^n \quad (2)$$

where x is the order with regard to the concentration of catalyst. When no external catalyst is present or when overall reaction rate is independent of catalyst concentration, $x = 0$, and eq.2 reduces to eq.1. Eq.2 indicates that if the removal of water affects the concentrations of acid and alcohol, it also affects that of the catalyst. If the changes in the concentrations of acid and alcohol due to the removal of water deserve consideration in kinetic equations, then the concentration of the catalyst should also be taken into account.

If the initial concentrations (moles/kg) of acid, alcohol and catalyst are denoted by a_0 , b_0 and c_0 , respectively, and their concentrations at time t by a , b , c , then the number of moles of water N_{water} that is generated at time t can be calculated from:

$$N_{\text{water}} = a_0M_0 - 0.018M, \quad N_{\text{water}} = b_0M_0 - 0.018M \quad (3)$$

where M_0 and M stand for the total mass of the charge at $t = 0$, and at time t , respectively. If water can be completely and instantaneously removed from the reaction system, then

$$M = M_0 - 0.018N_{\text{water}} \quad (4)$$

From eqs.3 and 4, the following equations can be easily derived:

$$\frac{M_0}{M} = \frac{1 - 0.018a}{1 - 0.018a_0} \quad (5)$$

$$b = a + (b_0 - a_0) \frac{1 - 0.018a}{1 - 0.018a_0} \quad (6)$$

The catalyst concentration at time t is:

$$c = \frac{M_0}{M} c_0 = \frac{1 - 0.018a}{1 - 0.018a_0} c_0 \quad (7)$$

The general kinetic equation taking the removal of water into consideration is then:

$$-\frac{da}{dt} = k_{water} \left(\frac{1-0.018a}{1-0.018a_0} c_0 \right)^x a^m \left(a + (b_0 - a_0) \frac{1-0.018a}{1-0.018a_0} \right)^n \quad (8)$$

where k_{water} stands for the corrected reaction rate constant.

We can notice that when $x = 0$, eq.9 is exactly the same as the one derived by Marechal, and thus his conclusions hold. But when x is not zero, the catalyst concentration must be corrected if the reaction is balanced stoichiometrically, and that of alcohol should also be corrected if it is non-stoichiometric.

If the removal of water is not taken into account, eq.9 becomes:

$$-\frac{da}{dt} = k c_0^x a^m (a + b_0 - a_0)^n \quad (9)$$

where k denotes the rate constant without correcting for the water removal.

The ratio of k_{water} and k can be obtained upon dividing eq.9 by eq.10:

$$\frac{k_{water}}{k} = \left(\frac{1 - 0.018a}{1 - 0.018a_0} \right)^{-x} \left(\frac{a + (b_0 - a_0) \frac{1 - 0.018a}{1 - 0.018a_0}}{a + b_0 - a_0} \right)^{-n} \quad (10)$$

where the first factor of the right side attributes to the catalyst, and the second one to alcohol. The first factor is always less than unity, and the second one is less than unity for $b_0 > a_0$ and larger than unity for $b_0 < a_0$. Thus the ratio k_{water}/k is less than unity for $b_0 > a_0$, which is the case for most kinetic studies reported in the literature. Furthermore, this ratio varies with the degree of reaction. This suggests that in some cases, neglecting the removal of water may lead to a misinterpretation of kinetic data.

COMPARISON OF THE GENERAL KINETIC EQUATION BETWEEN THE CONCENTRATIONS EXPRESSED IN MOLES/KG AND MOLES/LITER

Expressing a concentration in moles/kg or moles/l is a matter of preference. Unfortunately, this may be misleading, as is demonstrated below. We start with eq.2, which can be written either in the form of eq.11 or eq.12:

$$-\frac{1}{V} \frac{dN_a}{dt} = k_v \left(\frac{N_{cat}}{V} \right)^x \left(\frac{N_a}{V} \right)^m \left(\frac{N_b}{V} \right)^n \quad (\text{volume basis}) \quad (11)$$

$$-\frac{1}{M} \frac{dN_a}{dt} = k_M \left(\frac{N_{cat}}{M} \right)^x \left(\frac{N_a}{M} \right)^m \left(\frac{N_b}{M} \right)^n \quad (\text{mass basis}) \quad (12)$$

where N_a , N_b and N_c denote the molar quantities of acid, alcohol and catalyst, respectively, at time t ; V and M stand for the total volume and mass of the charge at time t . For distinction, the coefficients k_v and k_M represent volume and mass reaction rate constants.

Dividing eq.11 by eq.12 and rearranging yields the relation between k_v and k_M :

$$k_M = k_v \left(\frac{M}{V} \right)^{x+m+n-1} = k_v \rho^{x+m+n-1} \quad (13)$$

where ρ is the density of the charge.

It has been shown theoretically and proven experimentally (6) that the reaction rate is proportional to the volume concentrations of reactants and characterized by a real constant k_v for a reaction of a given mechanism. Thus k_M is not a real constant but a function of the charge density. The density of a polyesterification system usually increases with conversion, similar to a bulk free radical polymerization where the density of the whole system may increase from 10% to 25%. It is therefore conceivable that k_M may increase more significantly as the reaction progresses. This implies that for a correctly proposed mechanism, its rate constant k_M should not be a constant but most probably an increasing function of the degree of reaction. It should not be confused, however, that the change in charge density is not necessarily caused by the water removal. The removal of water and change in density are independent events, and they should be taken into account in the analysis of kinetic data.

CONCLUDING REMARKS

A general kinetic equation has been derived, showing that the one derived by Marechal is correct only when no external catalysts are present or when the rates of reaction are independent of the catalyst concentration. Moreover, it has been shown that the removal of water should be taken into account not only for the concentration of alcohol, but also for that of catalyst if it contributes to the overall rate of reaction. The rate constant thus obtained is smaller than that if the removal of water is neglected. On the other hand, it has been found that the rate constant using moles/kg is not a real constant, but a function of the density of the reaction mixture. In order to obtain true rate constants and to avoid misinterpretation of kinetic data, it is recommended to use volume concentrations (eq.12).

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