

A Kinetic and Equilibrium Model for Nylon 6,6 Polymerization

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Synopsis

A simple, activity-based solution model is used to develop thermodynamically proper correlation forms for the description of the rate and equilibrium behavior of nonideal polyamidations. The approach is especially useful in systems for which limited equilibrium and kinetic data are available. This model is applied to the nylon 6,6 system. The resulting correlation is valid for water concentrations from 1 to 90 mol% and for temperatures from 200 to 265°C. The equilibrium correlation is a function of the water mole fraction and temperature. At a fixed temperature, there is a maximum in the apparent equilibrium constant at a water concentration of approximately 10 mol%. There is an apparent inversion in the sign of the heat of amidation, as well as a continuous change in the apparent rate of polymerization from second to third order in carboxyl concentration at low water content.

INTRODUCTION

A nylon 6,6 polyamidation can be treated as a second-order reversible reaction



of an amine (A) and carboxyl (C) end-group to form an amide linkage (L), with the elimination of a water molecule (W). The thermodynamic rate and equilibrium constants are defined in terms of the activities of the four components¹

$$r = k a_A a_C - k' a_L a_W \quad (2)$$

$$K = \frac{k}{k'} = \frac{a_L a_W}{a_A a_C} \quad (3)$$

where r is the intrinsic reaction rate and k and k' are the forward and reverse reaction rate constants. These true thermodynamic rate and equilibrium constants only depend on temperature and a reference state.

An apparent equilibrium constant K_{app} and forward reaction rate constant k_{app} are defined as

$$K_{\text{app}} = \frac{x_L x_W}{x_A x_C} \quad (4)$$

and

$$k_{\text{app}} = \frac{r}{x_A x_C - \frac{1}{K_{\text{app}} x_L x_W}} \quad (5)$$

where x_i is the mole fraction of the i th constituent. Mole fractions have been used in eq. (5) rather than the usual concentrations because this eliminates the need for density correlations and because they are more fundamentally related to activities. The apparent and thermodynamic rate and equilibrium constants are related as follows:

$$k_{\text{app}} = k \gamma_A \gamma_C \quad (6)$$

where γ_A is the activity coefficient of component A ($a_A = \gamma_A x_A$) and

$$K_{\text{app}} = K/K_\gamma \quad (7)$$

where $K_\gamma = \gamma_A \gamma_C / \gamma_L \gamma_W$.

In an ideal solution, all the activity coefficients are unity, and the apparent and thermodynamic rate and equilibrium constants are identical. However, in nonideal solutions, the activity coefficients may deviate considerably from unity, and the apparent rate and equilibrium constants can exhibit a strong compositional dependence.

In principle, the composition dependence of the apparent rate and equilibrium constants could be resolved by carrying out enough experiments to determine the activity of all the relevant species, including those produced by side reactions, as functions of temperature, pressure, and composition. However, this approach is usually impractical. Nevertheless, it is advantageous to regress the available data in a thermodynamically consistent way. We show here that when only the rate and equilibrium constants are required, the composition dependence of the activities may be lumped into two independent groups, which depend only on the reactant and product activities. Hence, it is not necessary to determine the composition dependence of each component's activity separately.

The reaction equilibrium in polyamidations is such that the reaction must be driven by removal of the water in order to obtain high molecular weights. This removal of water during the course of the polymerization, along with the disappearance of polar end groups by reaction, causes the polarity of the reaction medium to change drastically. Even if one assumes that the equal reactivity hypothesis is valid, the apparent rate and the apparent equilibrium constants can depend on the instantaneous solution composition. In other words, the assumption that the end-group reactivity is independent of molecular size does not preclude its dependence on solution environment.

A fundamental molecular model that would be suitable for describing the behavior of nylon polycondensations over a wide range of variables is not currently available. This is presumably due to the complex nature of the problem arising from a highly nonideal liquid solution, the complex equilibria and the role of acid catalysis during polycondensation. In this paper we will show how a simple activity-based model can be used to determine the proper form of the apparent reaction rate and equilibrium correlations for nonideal polycondensations. This model is applied to the experimental data for the nylon 6,6 polyamidation.

A NONIDEAL LIQUID MODEL

During polyamidation, the polar nature of the end groups and the condensate causes the system to deviate considerably from ideal solution behavior, with activity coefficients that deviate substantially from unity. The temperature dependence of the activity coefficient is given by the standard thermodynamic relation²

$$d \ln \gamma_i = \left(-\overline{\Delta H}_i / RT^2 \right) dT \quad (8)$$

where $\overline{\Delta H}_i$ is the partial molar heat of mixing of component i . Equation (8) is strictly true at constant pressure and composition. If the true thermodynamic rate and equilibrium constants are written in terms of activities and eq. (8) is integrated assuming temperature independent heats of mixing, the following expressions for the apparent rate and equilibrium constants may be derived:

$$K_{app} = K_0 \exp \left[-\frac{\Delta H_{app}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (9)$$

$$k_{app} = k_0 \exp \left[-\frac{E_{app}}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (10)$$

where $\Delta H_{app} = \overline{\Delta H}_L + \overline{\Delta H}_W - \overline{\Delta H}_A - \overline{\Delta H}_C$, $E_{app} = -(\overline{\Delta H}_A + \overline{\Delta H}_C)$ and T_0 is an arbitrary reference temperature.

The quantities K_0 , k_0 , ΔH_{app} , and E_{app} may depend on all the mole fractions x_i ; only in an ideal solution are they all independent of composition. For a stoichiometrically balanced polycondensation, the composition dependence of these quantities can be a function of at most two of the independent mole fractions.

Also, one may develop the identical expression for k_{app} if both the forward and reverse reaction in eq. (1) are assumed to be acid-catalyzed. The apparent activation energy is then $E_{app} = -(\overline{\Delta H}_A + 2\overline{\Delta H}_C)$ and $k_0 = k'_0 x_C$. Thus, the second and third order kinetic models in these nonideal liquid mixtures cannot be distinguished based upon the available kinetic data without determining the activities of the individual constituents.

APPLICATION TO NYLON 6,6

Equilibrium Correlation

A decrease in the apparent equilibrium constant for nylon 6,6 polymerization with increasing water mole fraction ($x_w > 0.2$) was reported by Wiloth³ and Ogata.⁴ Giori and Hayes⁵ found that the apparent equilibrium constant for nylon 6 polymerization also increased with water content at mole fractions less than 10% and that it decreased at higher water contents in a manner consistent with the previous findings of Wiloth³ and Ogata⁴ for nylon 6,6. This increase in the apparent equilibrium constant at very low water content was also reported by Wiloth.⁶ Since nylon 6 and nylon 6,6 have identical ratios of methylene, carboxyl, amide, and amine groups at any conversion, it is expected that the ionic character of the reacting medium will be similar at a given composition (i.e., the same number of amide linkages, end groups, and water molecules). This suggests that the nylon 6,6 system might also exhibit similar reaction rate and equilibrium behavior. In fact, an apparent equilibrium constant of 250 for nylon 6,6 at very low water content (approximately 1 mol%) reported by Jacobs and Zimmerman⁷ and a value of 225 calculated from data presented by Jones and White⁸ are remarkably consistent with the value of 250 obtained by extrapolating the nylon 6 data of Giori and Hayes.⁵ Based on this observation, we include these data of Giori and Hayes⁵ in our equilibrium regression. This is also consistent with the commonly accepted "long-chain hypothesis," which has been verified in many systems.^{9,10}

Ogata¹¹ reported high temperature nylon 6,6 equilibrium studies at low water content. However, these were not included in the equilibrium regression because we suspect that degradation reactions were present during the prolonged (6 h) experiments. These data also disagree with those of Jacobs and Zimmerman⁷ and Jones and White.⁸ For the thermally sensitive nylon 6,6 the determination of the intrinsic polycondensation kinetics may actually be more accurately made based on data from the relatively stable nylon 6 system, which is less complicated by side reactions during extended high temperature studies. Wiloth⁶ showed that nylon 6 reaches equilibrium after about 80 h at 240°C at a water content of 0.4 wt %.

Kumar et al.¹² correlated the equilibrium data of Ogata⁴ using the form $K_{app} = \exp[a - b(W^0)]$, where (W^0) is the dimensionless initial water content (mol water/mol initial nylon salt), corresponding to mole fractions of water in the range 0.5–0.8; the temperatures were in the range 200–220°C. The values of a and b were determined as functions of T and (W^0) as shown in Table I of Kumar et al.¹² However, the dependence of the correlation on the initial condition renders it unacceptable for the study of continuous polyamidation reactions.

Although the apparent equilibrium constant can be a function of two of the independent component mole fractions, the data of Wiloth,³ Ogata,⁴ and Giori and Hayes⁵ clearly show that the mole fraction of water produced the predominant variation in the observed equilibrium constant. Thus, we regressed the apparent equilibrium correlation solely in terms of the mole fraction of water. The apparent heat of reaction was determined from the

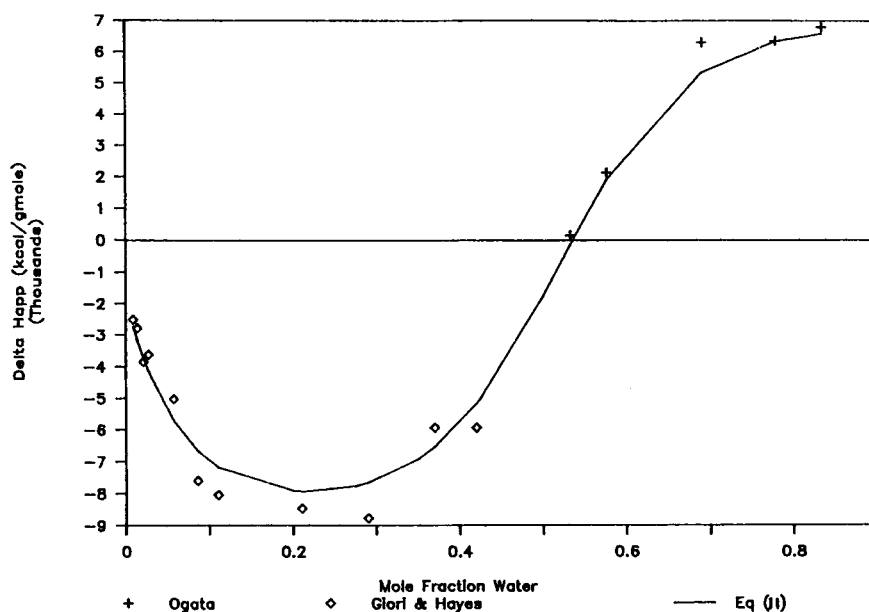


Fig. 1. Apparent enthalpy of reaction vs. mole fraction water.

combined data of Ogata⁴ and Giori and Hayes⁵ by evaluating $d(\ln K_{app})/dT$ as a function of x_w . The data are shown in Figure 1 along with the empirical correlation

$$\Delta H_{app} = 7650 \tanh[6.5(x_w - 0.52)] + 6500 \exp(-x_w/0.065) - 800 \quad (11)$$

Care was taken to fit the data at lower mole fractions of water data most accurately and not to greatly exceed the accepted heat of amidation for the reaction, which is 6–7 kcal/mol.^{7,8,13–15}

The reaction appears to be endothermic at water compositions greater than 52 mol %, and exothermic at lower concentrations. This is consistent with the observation of Ogata.⁴ However, we note that nonideal liquid phase behavior could provide a complete explanation of this inversion of the heat of reaction. It may be unnecessary to account for any "hydrolytic degradation of nylon 6,6" as suggested by Ogata,⁴ although such hydrolysis is not necessarily ruled out.

The prefactor K_0 is easily determined via eqs. (9) and (11) and the data. A reference temperature of 200°C was chosen arbitrarily. In this regression the data of Wiloth³ and the single points of Jacobs and Zimmerman⁷ and Jones and White⁸ were added to the data of Ogata⁴ and Giori and Hayes.⁵ The K_0 correlation is shown in Figure 2 and is given by the empirical equation

$$K_0 = \exp\{[1 - 0.47 \exp(-x_w^{1/2}/0.2)](8.45 - 4.2x_w)\} \quad (12)$$

The fact that all of the data can be described by a single curve, indicates that the nylon 6 equilibrium data is representative of the nylon 6,6 system and attests to the fact that the apparent equilibrium constant may be described

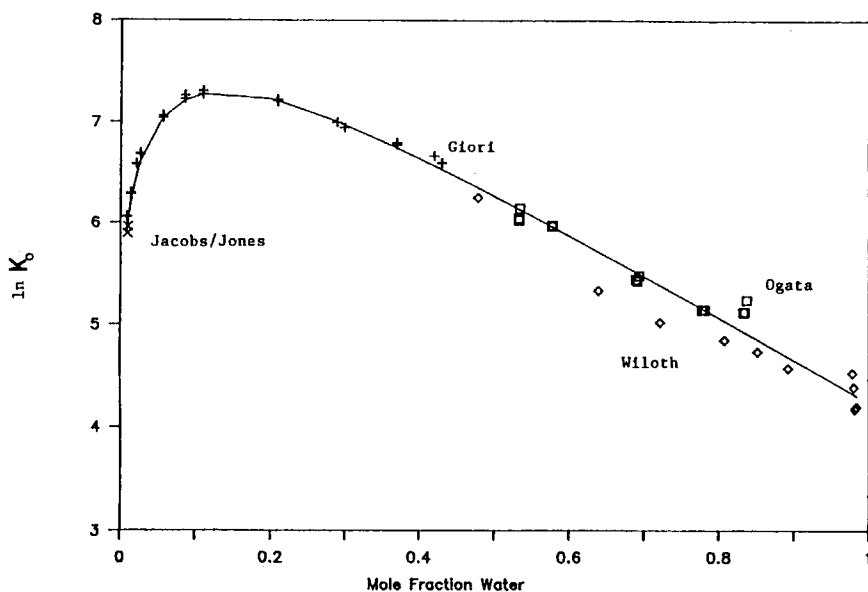


Fig. 2. Apparent equilibrium constant at 200° C vs. mole fraction water.

solely by the mole fraction of water and the temperature. This is surprising since two mole fractions are necessary to specify the stoichiometrically balanced polyamidation.

The final equilibrium correlation is given by eqs. (9), (11), and (12). Figures 3 and 4 compare the resulting correlation against the available published data. A more comprehensive view of the correlation is shown in Figure 5.

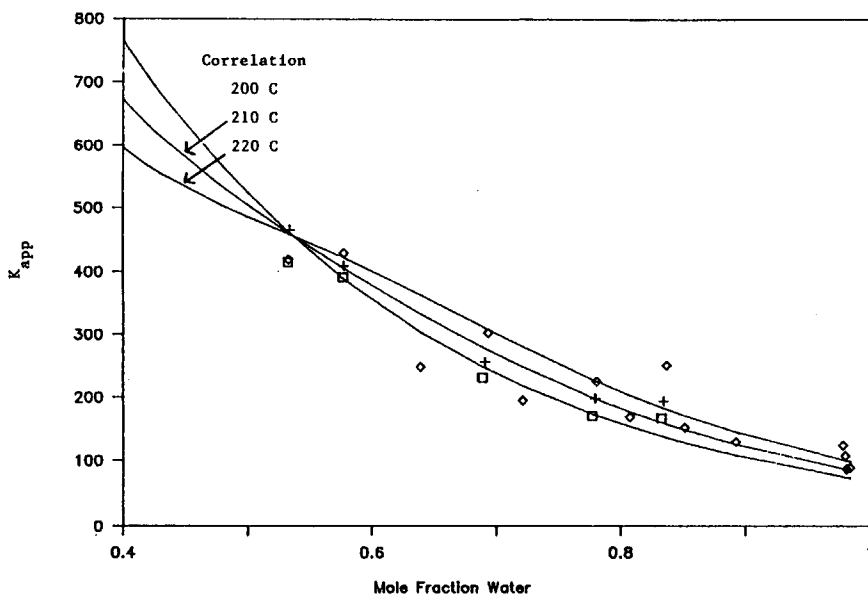


Fig. 3. Apparent equilibrium constant vs. mole fraction water: (□) Ogata 200° C; (+) Ogata 200° C; (◇) Ogata/Wiloth 220° C.

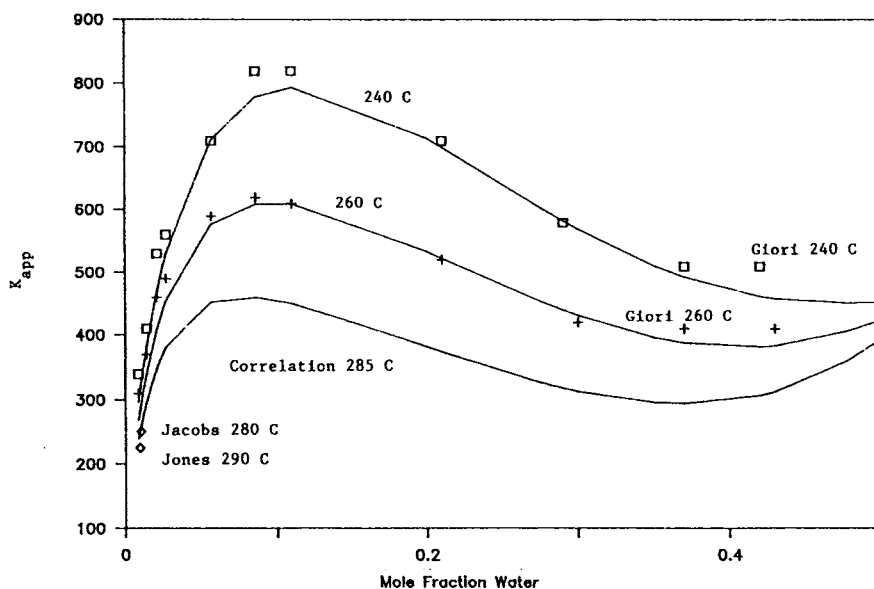


Fig. 4. Apparent equilibrium constant vs. mole fraction water.

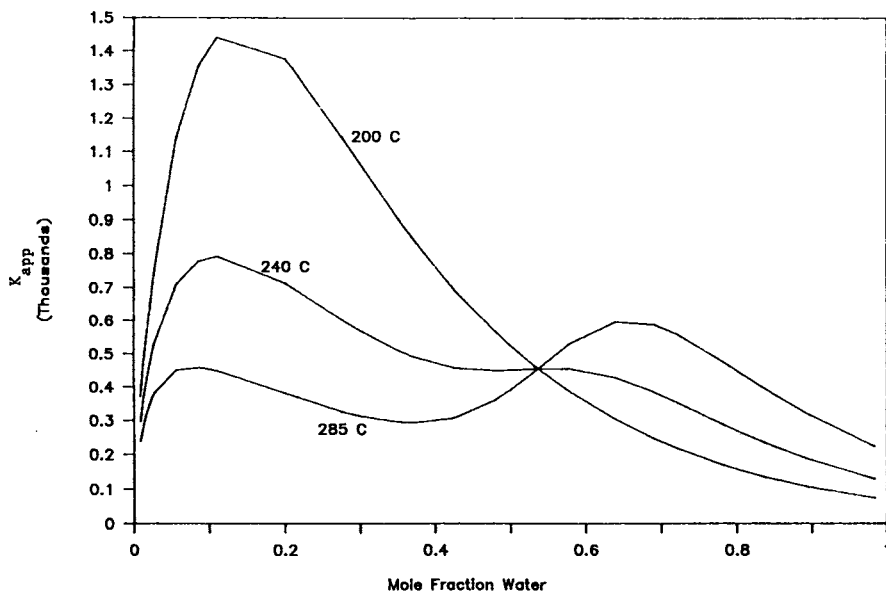


Fig. 5. Apparent equilibrium constant vs. mole fraction water.

REACTION RATE CORRELATION

Ogata⁴ published rate data and a correlation for the nylon 6,6 polymerization, which depends on the *initial* water content. Unfortunately, this dependence prevents its use in the study of continuous polycondensation. Furthermore, the regression was done under the assumption that K_{app} is constant, which is incorrect except over small ranges of temperature and

composition. Ogata⁴ reported the concentrations of end groups, water, and amide linkages at time intervals from 0.5 to 11 h, water mole fractions of 0.1–0.8, and at temperatures from 200 to 220°C. We regressed these data via a least squares integral analysis, using a value of K_{app} from our correlation. The total number of moles in the system was chosen as the extensive variable since eq. (1) conserves this quantity in closed batch experiments. Using a reference temperature of 200°C, eq. (10) reduces to $k_{app} = k_0$. Our calculations showed that Ogata's 200°C experiments at mole fractions of water less than 0.5 could be described by a single constant k_0 , whereas those with $x_w > 0.6$ could be described by another, smaller constant. Thus, k_0 changes rapidly at about $x_w = 0.55$ and was regressed as

$$k_0 = \exp\{2.55 - 0.45 \tanh[25(x_w - 0.55)]\} \quad (13)$$

We find that the rate constant changes rapidly in the same region where ΔH_{app} changes sign. The results were not very sensitive to the value of E_{app} over the range of the data, and a constant value of 21,000 cal/mol fitted all the data satisfactorily.

The validity of the equal reactivity assumption¹⁶ along with the slowing of the amidation rate at low water content, accompanied by a sensitivity to carboxyl concentration have been well documented. Studies which follow apparent second-order kinetics^{4,5} have been at high water contents. At lower water contents an acid-catalyzed mechanism is increasingly important.^{17–21} Although, virtually all of the low water content kinetic studies have been done on nylon 6, it is expected that the nylon 6,6 rate constant will be nearly identical to that of nylon 6 at low water concentrations, just as the equilibrium was found to be. We have therefore merged the high water content correlation of Ogata's⁴ data with that of Reimschuessel and Nagasubramanian²¹ to obtain a comprehensive reaction rate correlation.

It is impossible to identify a precise water concentration where the two correlations should crossover. However, it is clear that the reaction rate appears to be second order at high water content but has both second- and third-order character at low acid and low water content. Based on the lowest water content study of Ogata⁴ at 11 mol% and the highest water content study of Reimschuessel and Nagasubramanian²¹ at 8 mol%, we can expect a transition near 10 mol% water. This also corresponds to the point where ΔH_{app} increases rapidly, as shown in Figure 1.

It is important to realize that the majority of data for nylon 6 was taken at water mole fractions less than 0.08 because the reaction proceeds with a net consumption of water due to the caprolactam ring opening. Conversely, the nylon 6,6 reaction rapidly generates water so that the majority of data were taken at water content greater than 50%. It is expected that the correlation of Ogata's data is most accurate at $x_w > 0.3$ and Reimschuessel's and Nagasubramanian's correlation at $x_w < 0.05$. A transition near 0.1 represents the best available estimate, but could be easily adjusted with additional kinetic data.

Reimschuessel and Nagasubramanian²¹ regressed the kinetic rate constant as a linear combination of second- and third-order rate models. The rates of the two contributions were characterized by different activation energies. The

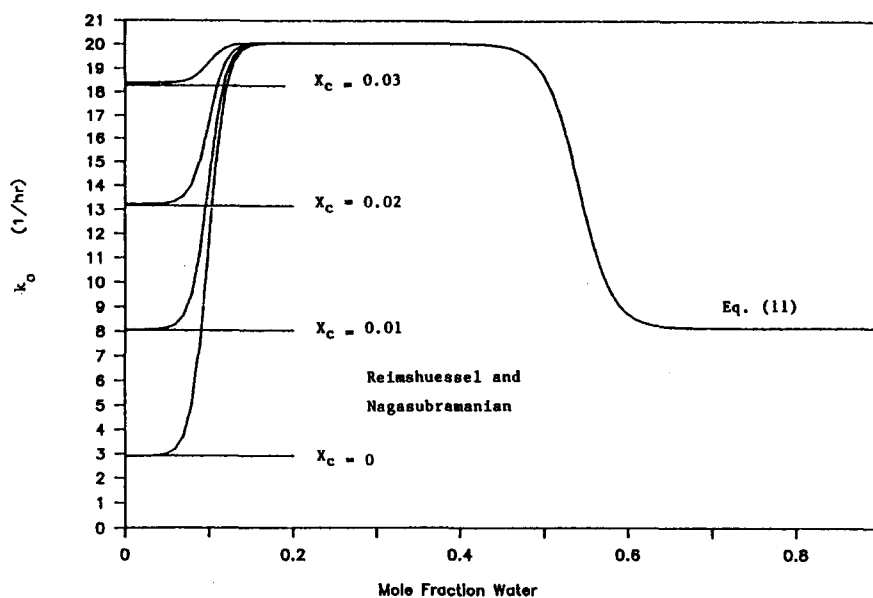


Fig. 6. Apparent rate constant at 200° C vs. mole fraction water.

constants of Reimschuessel and Nagasubramanian²¹ were converted to the same units as eq. (13) by assuming a value of the ratio (g polymer/mol amide linkages) for dry nylon 6 of infinite molecular weight, which is a good approximation to the experimental conditions. The final kinetic expression in eq. (10) requires a single activation energy and a constant of 21,400 cal/mol was used. This is the mean of the two values for the composite model and the

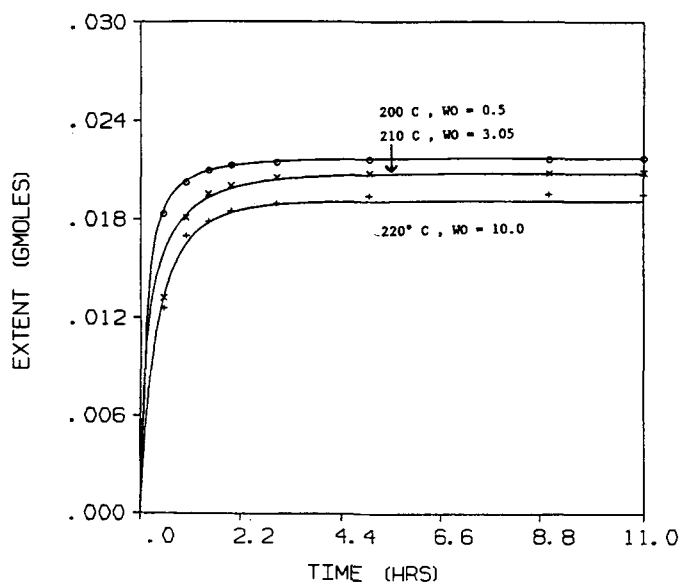


Fig. 7. Comparison of the simulation and the data of Ogata.⁴

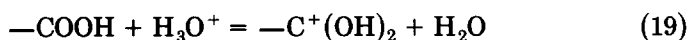
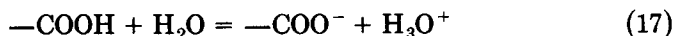
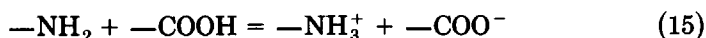
value of 21,000 cal/mol from Ogata's data. The final empirical expression is

$$k_0 = \exp\{2.55 - 0.45 \tanh[25(x_w - 0.55)]\} \\ + 8.58\{\tanh[50(x_w - 0.10)] - 1\}(1 - 30.05x_c) \quad (14)$$

The resulting k_{app} at 200°C is plotted vs. x_w at various x_c is Figure 6, along with the correlation of Reimschuessel and Nagasubramanian.²¹ Simulations using the final rate and equilibrium correlations are compared with some of the data of Ogata⁴ in Figure 7. The data of Reimschuessel and Nagasubramanian are valid up to 265°C. Therefore, the combined kinetic and equilibrium model has been tested up to 265°C, but the equilibrium correlation is valid up to 290°C.

DISCUSSION

The final equilibrium and kinetic correlations describe the available data well. Their complex mathematical form reflects both the nonideality of the liquid mixture and complex chemical and ionic interactions in the reacting medium. Some of the equilibria which are considered to be significant in the polyamidation system include^{8,22}



It is not surprising that the rate constant of eq. (16) should vary significantly with the mole fraction of acid and water in the system. The ionic character of the system changes drastically as it goes from a 50% salt solution to a dry, high molecular weight polymer and all the various equilibria are affected. A more accurate simulation would have to consider some or all of these equilibria and estimate the activities of all species, including ionic moieties, as functions of the solution composition and temperature.

The reason that the apparent equilibrium constant should vary so markedly with the mole fraction of water may be qualitatively explained by Flory-Huggins theory.¹⁰ If water is considered to be a low molecular weight solvent for nylon 6,6, the theory predicts that the activity of the water will vary nonlinearly with its volume fraction. Since the thermodynamic equilibrium constant is fundamentally a ratio of activities (which Flory has established are not directly proportional to mole fractions), the apparent equilibrium constant is not expected to be concentration independent.

Figures 4 and 5 show that the apparent equilibrium constant goes through a maximum at a water concentration of 10 mol%. The effect becomes less pronounced with increasing temperature. Whether or not the low temperature equilibrium ($< 240^{\circ}\text{C}$) can ever be reached remains to be seen. At lower temperatures and higher molecular weights crystal formation and diffusional effects may virtually stop the reaction. If one is interested in very high molecular weight nylon 6,6, our results suggest 10% mol fraction water and lower temperatures will yield the most fruitful results.

The model from which the correlations were derived is not restricted to nylons or polymers in general. The model may be applied to any second-order reversible reaction. It is particularly useful for nylons because the polyamidation takes place over such a wide range of composition in a highly nonideal medium. Another class of polymers where we expect the model to be useful is polyesters; like nylons, there is some controversy as to the reaction order of the polymerization.²³

CONCLUSIONS

The simple model has been shown to be effective for correlating limited equilibrium and rate data for a highly nonideal polyamidation. The model, although useful for obtaining engineering correlations and for design and control purposes, really gives little insight into molecular mechanisms which are responsible for the apparent change in order of the reaction. It does suggest that the change in the apparent order of the reaction may simply be the manifestation of nonideal liquid solution effects. The model may be easily applied to other polycondensation systems.

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APPENDIX: NOMENCLATURE

A	amine group
α_i	activity of component i
C	carboxyl group
E_{app}	apparent activation energy (cal/mol)
ΔH_{app}	apparent enthalpy of reaction (cal/mol)
$\Delta \bar{H}_i$	partial molar heat of mixing of component i (cal/mol)
k, k'	thermodynamic forward and reverse reaction rate constant (mol/total mol h)
k_{app}	apparent forward reaction rate constant (mol/total mol h)
k_0	reference apparent forward rate constant (mol/total mol h)
K_{app}	apparent equilibrium constant, dimensionless
K_0	reference apparent equilibrium constant, dimensionless
K_γ	$\gamma_A \gamma_C / \gamma_L \gamma_W$, dimensionless
L	amide linkage
r	intrinsic reaction rate (mol/total mol h)
R	gas constant (1.987 cal/mol K)
T	temperature (K)
T_0	reference temperature, 473 K
W	water molecule
W^0	initial water content (mol water/mol initial salt)
x_i	mole fraction of component i , dimensionless
γ_i	activity coefficient ($\alpha_i = \gamma_i x_i$) component i , dimensionless

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