Periodic behaviour in continuous emulsion polymerization systems

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A modification of the model of Brooks for a non-steady-state continuous emulsion polymerization reaction has been examined to ascertain whether it permits the possibility of (a) periodic fluctuations in rate of polymerization in the vicinity of the steady state, and (b) sustained fluctuations in rate of polymerization in any physically-attainable condition. We conclude that neither of these possibilities is realizable in reaction systems which conform to the model which has been considered. Nor are sustained oscillations possible in reaction systems which conform to certain variants of the model.

INTRODUCTION

Increasing interest is being shown in the use of continuous reactors for the production of polymers by emulsion polymerization. As a consequence, attempts are being made to understand the main features of continuous emulsion polymerization reactions in terms of those ideas which have proved useful in understanding the behaviour of reactions carried out in batch reactors.

In general, attempts to understand the behaviour of continuous emulsion polymerization reactions have been confined to consideration of the steady-state behaviour of the reaction system[1,2]. Transient effects which arise during the start-up stage of the reaction have not received such close attention. This is hardly surprising, since the proportion of the total output of polymer which is produced during the start-up period is usually small. Some experimental studies[3,4] have indicated that, in certain circumstances, the ultimate behaviour of continuous emulsion polymerization reactions can be such that the rate of polymerization persistently oscillates. Apart from the inherent interest in the possibility of this phenomenon, it is also of considerable practical interest, in that, were such periodic fluctuations in polymerization rate to occur, they might well be accompanied by similar periodic fluctuations in the properties of the polymer which is produced.

The origin of these persistent fluctuations in polymerization rate is unclear. Gerrens and Kuchner[1] have pointed out that variations in the rate of feed of the reactants could be one cause, but it should clearly be possible to eliminate fluctuations arising from this cause by carefully controlling the feed rates of the reactants. Variations arising from this kind of cause are not the subject of this paper. Our purpose is to examine a plausible model for a continuous emulsion polymerization in order to ascertain whether the model allows the inherent possibility of periodic fluctuations in polymerization rate. The model which has been considered is essentially that proposed by Brooks[5] for non-steady-state emulsion polymerization, with some additional assumptions noted below. Some experimental evidence in support of some of the supposed conclusions drawn from the model has been presented in a recent paper by Brooks, Kropholler and Purt[4].

MODEL CONSIDERED HERE

The emulsion polymerization reaction is assumed to be taking place in a single well-stirred reactor, so that effects arising from macroheterogeneity within the reaction system can be neglected. Reactants are assumed to be fed into the reactor at steady rates, and the reaction product is being removed at a steady rate, such that the volume of reactants in the reactor remains constant. The monomer and surfactant solution are assumed to be fed in separately from the initiator solution, so that polymer particles can be assumed to be absent from the feed. The monomer is assumed to be only sparingly soluble in water, and the surfactant to be present in the initial feed at a concentration above its critical micelle concentration. Thus particles are assumed to be formed exclusively by micellar nucleation; complications arising from the simultaneous occurrence of homogeneous nucleation are ignored. The monomer is assumed to be completely miscible with its polymer, and to be present in sufficient quantity so as to ensure that an excess of monomer is present as droplets at all stages of the reaction.

All these criteria were probably satisfied in the experiments reported by Brooks, Kropholler and Purt[4] for the emulsion polymerization of styrene in a continuous stirred reactor at 50°C. In particular, the results reported for peak and steady-state conversions suggest that in most of the experiments excess monomer was present as a droplet phase throughout the entire course of the reaction. The significance of this observation is that the concentration of monomer at the reaction locus probably remained constant throughout the reaction, and consequently any periodic fluctuations in reaction rate which were observed cannot have been due to fluctuations in the concentration of monomer at the reaction locus. Thus in order to account for periodic fluctuations in polymerization rate, it is necessary

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that the model should allow the possibility of periodic fluctuations in either (i) particle number or (ii) average number of propagating radicals per reaction locus. The assumption is made here that the average number of propagating radicals per reaction locus does not fluctuate significantly as the reaction proceeds, and so the enquiry reduces to a consideration of the possibility of periodic fluctuation in particle number. It is recognized, however, that the assumption of a constant average number of propagating radicals per reaction locus may not in fact accord with reality.

According to Brooks, Kropholler and Purt[4], the Brooks model does permit the possibility of oscillations in polymerization rate. The root cause is said to be that the incoming surfactant micelles participate in two competing processes, namely, the nucleation of new particles and dissolution into the aqueous phase as monomolecular surfactant molecules. The tendency for the second of these processes to occur arises because the concentration of monomolecular surfactant has been reduced below its critical micelle concentration owing to the removal of surfactant molecules by adsorption at the surface of older particles which are growing in the reactor. If the rate of increase of particle surface area due to growth is greater than the rate at which particle surface area is lost from the reaction system by efflux of particles from the reactor, then the adsorption area available to surfactant molecules in the reactor will increase, and the rate of production of new particles will be expected to decrease. The rate of polymerization would then fall. It is postulated that, in some cases, the reduction in particle number may be such that the particle number 'undershoots' the steady-state value, and then subsequently increases to, and remains at, the steady-state value. In other cases, the particle number can continue to oscillate with respect to time. Brooks states that it may be difficult to distinguish in practice between these two types of behaviour. It is not entirely clear what are the factors which determine whether or not a steady-state is eventually achieved. However, if sustained oscillations do occur, their cause is attributed to a feedback effect which the products of the reaction (the particles) have upon the reaction process.

ANALYSIS OF THE MODEL

Differential equations for particle number and micelle number

For convenience, we use the same notation as Brooks[5]. The model gives the following expression for the rate of change with time of the number of particles (N) contained in unit volume of aqueous phase of the reaction system:

$$\frac{\mathrm{d}N}{\mathrm{d}t} = \frac{k_2 R_i N_m}{k_2 N_m + k_3 N} - \frac{N}{T} \tag{1}$$

where N_m is the number of surfactant micelles per unit volume of aqueous phase in the reaction system; R_i is the rate of acquisition of radicals from the aqueous phase by both the particles and the micelles which are present in unit volume of aqueous phase; k_2 and k_3 are rate coefficients for the processes of radical capture by micelles and by particles, respectively; t is time of reaction; and T is the mean residence time of the reactants in the reactor. This equation merely asserts that the overall rate of accumulation of new particles is equal to the difference between the rate of formation of new particles by micellar nucleation and the rate of loss of particles by efflux from the reactor. The rate of acquisition of radicals by particles and micelles is assumed to be first order in the concentration of the respective species. The rate coefficients k_2 and k_3 are assumed to be proportional to the respective areas of a single micelle and a single particle. Thus k_3 will depend upon the distribution of particle sizes which is present in the reactor at any instant, and will therefore be time-dependent during non-steady operation. However, to the extent that we are concerned with the behaviour of the reaction system in the vicinity of the steady state, we make the assumption that any variations in k_3 which occur are of negligible significance. Again, it must be recognized that this assumption may not be justified.

The rate of change with time of the number of micelles (N_m) contained in unit volume of aqueous phase of the reaction system is assumed to be given by the balance of contributions from four processes:

(i) entry of micelles into the reaction system from the surfactant feed solution;

(ii) removal of micelles from the reaction system by efflux;

(iii) dissociation of micelles into monomolecular surfactant molecules;

(iv) conversion to particles by micellar nucleation.

The following equation is obtained for the overall rate of accumulation of micelles in unit volume of the aqueous phase of the reaction system:

$$\frac{\mathrm{d}N_m}{\mathrm{d}t} = \frac{N_{m_0}}{T} - \frac{N_m}{T} - k_1 N_m - \frac{k_2 R_i N_m}{k_2 N_m + k_3 N} \tag{2}$$

where N_{m_0} is the number of surfactant micelles in unit volume of the surfactant solution which is being fed into the reaction system; and k_1 is the rate coefficient for the dissociation of micelles into monomolecular surfactant molecules. The four factors on the right-hand side of equation (2) arise, respectively, from the processes (i)–(iv) listed above. It should be noted that the process of micelle dissociation is assumed to be first order in number of micelles. This is equivalent to the assumption that micellar dissociation is a quasi-unimolecular process. We also note that equation (2) assumes the rate of formation of micelles from monomolecular surfactant species to be negligible; this is a reasonable assumption if the concentration of monomolecular species in the aqueous phase is significantly below the critical micelle concentration.

We now put $\tau = t/T$ (so that τ is the time of reaction relative to the mean residence time), $\alpha = k_3/k_2$, $\beta = 1 + k_1 T$, and $\gamma = R_i T$. The equations (1) and (2) then become, respectively:

$$\frac{\mathrm{d}N}{\mathrm{d}\tau} = \frac{\gamma N_m}{N_m + \alpha N} - N \tag{3}$$

and

$$\frac{\mathrm{d}N_m}{\mathrm{d}\tau} = N_{m_0} - \beta N_m - \frac{\gamma N_m}{N_m + \alpha N} \tag{4}$$

Thus for the model assumed, the variation of N with t during the non-steady state is determined by the solution of these two simultaneous non-linear first-order ordinary differential equations for N and N_m. Unfortunately, no general solution to this pair of simultaneous differential equations is readily available. However, there is a substantial corpus of essentially qualitative theory which is applicable to pairs of simultaneous differential equations of this type[6,7]. It will appear subsequently that by application of this theory it is possible to draw some significant conclusions concerning the behaviour of the model assumed here.

Representation of behaviour of reaction system as a trajectory in an N–N$_m$ *phase plane*

In the theory referred to above, N and N_m are regarded as defining orthogonal Cartesian axes in a two-dimensional space, called the 'phase plane'. Solutions of a given pair of differential equations will trace out paths, called 'trajectories', in this plane as time elapses. The steady state for the reaction is represented by the point for which $dN/d\tau = 0$ and $dN_m/d\tau = 0$. Thus the coordinates $(\bar{N}, \bar{N}_m)$ of the point which represents the steady state must obey the relationships:

$$\frac{\gamma\bar{N}_m}{\bar{N}_m + \alpha\bar{N}} - \bar{N} = 0 \tag{5}$$

and

$$\bar{N}_{m_0} - \beta\bar{N}_m - \frac{\gamma\bar{N}_m}{\bar{N}_m + \alpha\bar{N}} = 0 \tag{6}$$

These two equations are readily transformed into the pair:

$$\bar{N}_m = \frac{N_{m_0} - \bar{N}}{\beta} \tag{7}$$

and

$$\bar{N}_m = \frac{\alpha\bar{N}^2}{\gamma - \bar{N}} \tag{8}$$

Thus the points in the phase plane which represent steady states for the reaction system are the points of intersection of the two curves:

$$N_m = \frac{N_{m_0} - N}{\beta} \tag{9}$$

and

$$N_m = \frac{\alpha N^2}{\gamma - N} \tag{10}$$

These two curves are illustrated in *Figure 1a* (for the case

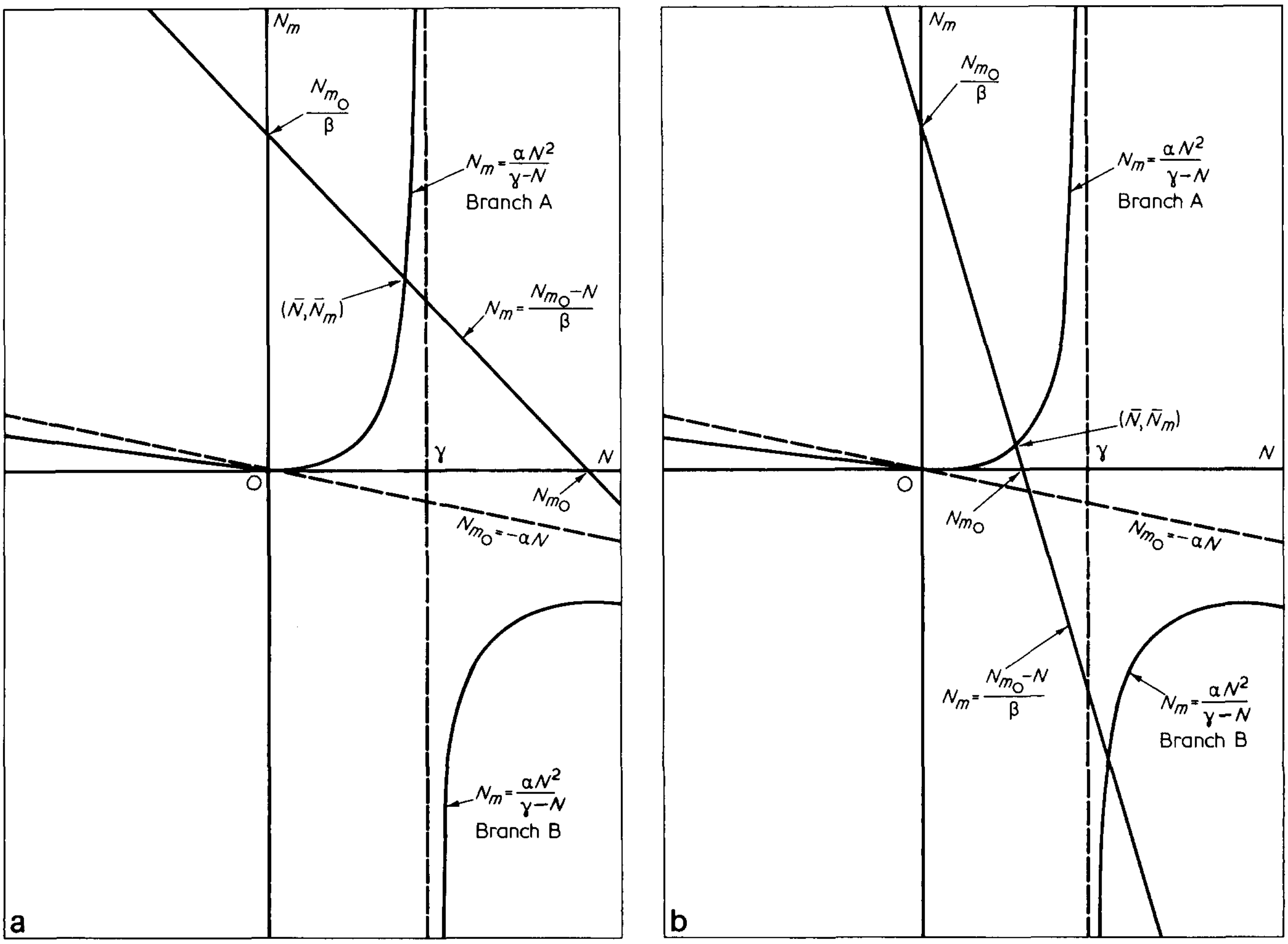

Figure 1 Illustrating the loci of the curves: $N_{m_0} = (N_{m_0} - N)/\beta$ and $N_m = \alpha N^2/(\gamma - N)$ in the N–N_m phase plane for the two cases: (a) $\gamma < N_{m_0}$; (b) $\gamma > N_{m_0}$

$\gamma < N_{m_0}$) and *Figure 1b* (for the case $\gamma > N_{m_0}$). The curve represented by equation (10) has two branches (marked A and B in *Figure 1*). However, only branch A need be considered, since only points lying in the first quadrant (N, $N_m \geqslant 0$) have physical significance, and branch B lies entirely in the fourth quadrant.

Thus the points in the phase plane which represent physically-realizable steady states for the reaction system are the points of intersection of the curve (9) and the branch A of curve (10) which lies in the first quadrant. In accordance with expectation, there is only one such point. Furthermore, limits can be set for the values of $\bar{N}$ and $\bar{N}_m$ as follows:

$$0 \leqslant \bar{N} \leqslant \min(N_{m_0}, \gamma) \qquad (11)$$

and

$$0 \leqslant \bar{N}_m \leqslant N_{m_0}/\beta \qquad (12)$$

where $\min(N_{m_0}, \gamma)$ denotes the lesser of N_{m_0} and γ.

Some information concerning the nature of the steady-state point ($\bar{N}$, $\bar{N}_m$) can be obtained by examining the behaviour of the trajectories on the boundaries of the physically-relevant region, i.e., a region bounded by the straight lines $N = 0$, $N_m = 0$, and the first quadrant of the circle $N^2 + N_m^2 = \rho^2$, where ρ is large compared with either N_{m_0} or N_{m_0}/β. It can be argued on general physical grounds that all the trajectories must be directed inwards at the boundaries of the physically-relevant region, because it can be surmized that systems which are represented by points remote from ($\bar{N}, \bar{N}_m$) must always tend to move towards the state represented by the point ($\bar{N}, \bar{N}_m$). The truth of this conclusion can be confirmed from equations (3) and (4) if α is constant, by considering the signs of $\mathrm{d}N/\mathrm{d}\tau$ and $\mathrm{d}N_m/\mathrm{d}\tau$ at various points on the boundary of the region, and hence inferring from the ratio $\mathrm{d}N_m/\mathrm{d}N$, $= (\mathrm{d}N_m/\mathrm{d}\tau)/(\mathrm{d}N/\mathrm{d}\tau)$, what must be the slopes of the trajectories at the various points on the boundary. A consequence of the trajectories being always directed inwards at the boundaries is that the system of trajectories must have a Poincaré index of +1. This in turn implies that the steady-state point must be a focus, a node, or a centre.

Behaviour of reaction system in vicinity of steady-state point

We now introduce the new variables

$$\theta = N - \bar{N} \quad \text{and} \quad \phi = N_m - \bar{N}_m \qquad (13)$$

The introduction of these variables is equivalent to transforming the critical point to the origin. In terms of these new variables, equations (3) and (4) become:

$$\frac{\mathrm{d}\theta}{\mathrm{d}\tau} = \frac{\gamma(\phi + \bar{N}_m)}{\phi + \bar{N}_m + \alpha(\theta + \bar{N})} - (\theta + \bar{N}) \qquad (14)$$

and

$$\frac{\mathrm{d}\phi}{\mathrm{d}\tau} = N_{m_0} - \beta(\phi + \bar{N}_m) - \frac{\gamma(\phi + \bar{N}_m)}{\phi + \bar{N}_m + \alpha(\theta + \bar{N})} \qquad (15)$$

In order to examine the behaviour of the trajectories in the vicinity of the steady-state point, we expand these expressions for $\mathrm{d}\theta/\mathrm{d}\tau$ and $\mathrm{d}\phi/\mathrm{d}\tau$ about the point $\theta = \phi = 0$, and neglect terms in θ and ϕ of higher order than the first. Taking into account the relationships (7) and (8) (or equivalently that both $\mathrm{d}\theta/\mathrm{d}t$ and $\mathrm{d}\phi/\mathrm{d}t$ must be zero at the point $\theta = \phi = 0$), it is found that

$$\frac{\mathrm{d}\theta}{\mathrm{d}\tau} \cong -\left\{1 + \frac{\alpha}{\gamma}\frac{\bar{N}^2}{\bar{N}_m}\right\}\theta + \frac{\bar{N}}{\bar{N}_m}\left\{1 - \frac{\bar{N}}{\gamma}\right\}\phi \qquad (16)$$

and

$$\frac{\mathrm{d}\phi}{\mathrm{d}\tau} \cong -\frac{\alpha}{\gamma}\frac{\bar{N}^2}{\bar{N}_m}\theta + \left\{\frac{\bar{N}^2}{\gamma\bar{N}_m} - \frac{\bar{N}}{\bar{N}_m} - \beta\right\}\phi \qquad (17)$$

Thus the behaviour of the reaction system in the vicinity of the steady state can be approximately described by the above two simultaneous linear first-order ordinary differential equations in θ and ϕ. The solutions to these equations can be written down immediately in terms of the eigenvalues λ_1 and λ_2, and the corresponding column eigenvectors, $[A_1]$ and $[A_2]$, of the matrix:

$$\begin{bmatrix} -1 - \dfrac{\alpha}{\gamma}\dfrac{\bar{N}^2}{\bar{N}_m} & \dfrac{\bar{N}}{\bar{N}_m}\left\{1 - \dfrac{\bar{N}}{\gamma}\right\} \\ -\dfrac{\alpha}{\gamma}\dfrac{\bar{N}^2}{\bar{N}_m} & \dfrac{\bar{N}^2}{\gamma\bar{N}_m} - \dfrac{\bar{N}}{\bar{N}_m} - \beta \end{bmatrix}$$

The general solution to the equations (16) and (17) is then (in matrix form)

$$\begin{bmatrix} \theta \\ \phi \end{bmatrix} = c_1[A_1]\,\mathrm{e}^{\lambda_1\tau} + c_2[A_2]\,\mathrm{e}^{\lambda_2\tau} \qquad (18)$$

where c_1 and c_2 are arbitrary constants.

The nature of the variation of θ and ϕ with τ is determined by λ_1 and λ_2. These in turn are the roots of the determinantal equation:

$$\begin{bmatrix} -1 - \dfrac{\alpha}{\gamma}\dfrac{\bar{N}^2}{\bar{N}_m} - \lambda & \dfrac{\bar{N}}{\bar{N}_m}\left\{1 - \dfrac{\bar{N}}{\gamma}\right\} \\ -\dfrac{\alpha}{\gamma}\dfrac{\bar{N}^2}{\bar{N}_m} & \dfrac{\bar{N}^2}{\gamma\bar{N}_m} - \dfrac{\bar{N}}{\bar{N}_m} - \beta - \lambda \end{bmatrix} = 0 \qquad (19)$$

From this, it follows that:

$$\lambda_1\lambda_2 = (\alpha\beta - 1)\frac{\bar{N}^2}{\gamma\bar{N}_m} + \frac{\bar{N}}{\bar{N}_m} + \beta \qquad (20)$$

from which $\lambda_1\lambda_2 > 0$, i.e. the real parts of λ_1 and λ_2 have the same sign. That $\lambda_1\lambda_2 > 0$ follows from equation (20) because $\beta = 1 + k_1T$, is always >1, and $\alpha = k_3/k_2$, is also always >1 (since the surface area of a particle must always be greater than that of a surfactant micelle). It also follows from equation (19) that:

$$\lambda_1 + \lambda_2 = -\left\{1 + \beta + \frac{\bar{N}}{\bar{N}_m} + \frac{\bar{N}^2}{\gamma\bar{N}_m}(\alpha - 1)\right\} \qquad (21)$$

so that $\lambda_1 + \lambda_2 < 0$. Thus taken with $\lambda_1\lambda_2 > 0$, this gives that λ_1 and λ_2 are both <0 if λ_1 and λ_2 are real, and that their real parts are negative if λ_1 and λ_2 are complex. In either event, equation (18) shows that the steady state is always stable, since the trajectory for any system slightly disturbed from the steady state must always be such that the system tends to return to the steady state. This conclusion follows regardless of the values of $\bar{N}$,$\bar{N}_m$, or any of the parameters which govern the behaviour of the assumed model.

We have therefore reached the conclusion that the model considered here carries the following implications:

(i) all the trajectories at the boundaries of the physically-relevant region of the $N - N_m$ phase plane are directed inwards;

(ii) the steady-state is stable.

The second of these conclusions rules out the possibility that the point representing the steady state can be surrounded by a closed trajectory of small amplitude. We therefore reach the conclusion that the model considered here does not permit the possibility of a periodic approach to the steady state. This does not mean that periodic solutions are necessarily excluded from the whole of the physically-relevant region, but it does mean that the phase plane would have to have a more complex structure than has been envisaged hitherto if it is to accommodate such closed trajectories. Indeed, taking conclusions (i) and (ii) above together, it seems inherently unlikely that the model allows periodic fluctuations of any magnitude about any point of the phase plane. However, there is a further general theorem which we can apply in order to show that the model considered here does not allow the possibility of sustained cyclic behaviour in any part of the physically-relevant region. However, before proceeding to these considerations, it is desirable to emphasize the following points concerning the preceding analysis.

(i) The linearized equations which have been used above are valid only in the immediate vicinity of the steady-state point. The behaviour of real reaction systems which are apparently quite close to the steady-state may not in fact be accurately represented by the linearized equations.

(ii) The above analysis, and the conclusions which have been drawn from it, may be invalid if the value of k_3 is not constant but fluctuates sufficiently over the region in the vicinity of the steady-state point.

(iii) The elimination of closed trajectories in the phase plane, corresponding to sustained oscillations, does not exclude the possibility of the existence of spiral trajectories into the steady-state point. A spiral trajectory of this type would correspond to damped oscillations about the steady state.

Possibility of sustained oscillations

The general theorem to which we have referred above is that of Dulac. This states that, for a system which is governed by a pair of autonomous non-linear ordinary differential equations:

$$\frac{dx}{dt} = P(x, y), \quad \frac{dy}{dt} = Q(x, y) \tag{22}$$

there cannot be any closed trajectories within a region R of the phase plane if the function:

$$\frac{\partial P}{\partial x} + \frac{\partial Q}{\partial y}$$

is of constant sign throughout R.

For a system which conforms to the model being considered here, the relevant equations are (3) and (4). We note that the right-hand sides of these equations are well-behaved at all points in the phase plane except those which lie on the line $N_m = -\alpha N$ (shown in *Figures 1a* and *1b*), but this line does not pass through the region which has physical significance. The theorem may therefore be applied to all points within the physically-relevant region except the single point $N = N_m = 0$. Denoting the right-hand sides of equations (3) and (4) by $P(N, N_m)$ and $Q(N, N_m)$, respectively, we have:

$$\frac{\partial P}{\partial N} = -\frac{\alpha\gamma N_m}{(N_m + \alpha N)^2} - 1, <0 \tag{23}$$

and

$$\frac{\partial Q}{\partial N_m} = -\beta - \frac{\alpha N}{(N_m + \alpha N)^2}, <0 \tag{24}$$

It therefore follows that both $\partial P/\partial N$ and $\partial Q/\partial N_m$ are negative for all physically-relevant values of N and N_m. We note that the signs of these quantities are not affected by the magnitude of $\alpha(=k_3/k_2)$, since α must always be positive. We therefore conclude that, if k_3 (and therefore α) is assumed to be constant for all values of N and N_m, as is the case for the model we are considering, the function:

$$\frac{\partial P}{\partial N} + \frac{\partial Q}{\partial N_m}$$

is negative throughout the entire region of physically-relevant values of N and N_m. The physically-significant region of the phase plane cannot therefore contain closed trajectories, and the model does not allow the possibility of sustained cyclic behaviour of any reaction system which conforms to it.

EFFECTS OF POSSIBLE MODIFICATIONS TO THE MODEL

It appears that none of the more obvious modifications which might be made to the model affects the general conclusion reached in the previous section that the N–N_m phase plane cannot contain closed trajectories.

A possible cause for cyclic fluctuations in particle number would be the occurrence of particle agglomeration. The simplest possible case to envisage is that in which particle agglomeration is kinetically of second order in particle number. Equation (3) would then be modified to become of the form:

$$\frac{dN}{d\tau} = \frac{\gamma N_m}{N_m + \alpha N} - \mathrm{N} - \epsilon N^2 \tag{25}$$

where ϵ is a constant. It is readily shown that $\partial P/\partial N$ is still always negative. A refinement of this modified model would be one which makes allowance for the fact that the probability of two colliding particles subsequently agglomerating almost certainly depends upon the degree of saturation of the particle surfaces with surfactant. If this is the case, then the parameter ϵ will vary with the position of the reaction system in the phase plane. A plausible way to make allowance for this effect would be to set $\epsilon = \epsilon' N/N_m$, where ϵ' is a constant. The contribution to $dN/d\tau$ from particle agglomeration would now be of the form $\epsilon' N^3/N_m$, but this will not affect the sign of $\partial P/\partial N$.

We also note that our conclusions are unaffected if equation (4) is replaced by an equation of the form:

$$\frac{dN_m}{d\tau} = N_{m_0} - \beta' N - \frac{\gamma N_m}{N_m + \alpha N} \qquad (26)$$

since $\partial Q/\partial N_m$ is still negative. The physical significance of this modification is, however, not entirely clear.

A further possibility is that periodic fluctuations become possible if the quantity k_3 (and therefore α) varies significantly with the position of the reaction system in the N–N_m phase plane. If periodic fluctuations did arise from this cause, they would presumably have to be of large amplitude, in order that significant changes in k_3 could occur in the course if the system traversing the closed trajectories implied by periodic solutions. Furthermore, the conclusions which have so far been reached concerning the nature of the N–N_m phase plane suggest that, in order to ensure continuity of the trajectories, there would have to be at least two periodic solutions of large amplitude if there were one. One of the two, that of lesser amplitude, would have to be unstable, and the other, that of greater amplitude, would have to be stable and its trajectory would also have to surround that which represented the unstable solution. A N–N_m phase plane of this rather complex structure seems to be inherently unlikely on physical grounds.

Still further possibilities are that (i) periodic fluctuations might become possible if allowance is made for the first-order loss of radicals from reaction loci by diffusion into the external phase; and (ii) periodic fluctuations might arise from variations in the rate of production of radicals caused by variations in the concentration of monomolecular surfactant molecules. It is relevant to the second of these possibilities that certain surfactants are known to affect the rate of thermal decomposition of initiators such as potassium persulphate.

CONCLUSIONS

Having examined a simple model for a continuous emulsion polymerization reaction, we conclude that this model does not permit the possibility of either periodic fluctuations in rate of polymerization in the vicinity of the steady state, nor of sustained fluctuations in rate of polymerization in any physically-realizable condition. Nor are sustained oscillations possible in reaction systems which conform to certain of the more obvious variants of the model. To the extent that reproducible periodic fluctuations in rate of polymerization are observed in continuous emulsion polymerization reactions, the explanation must be sought elsewhere than in conformity to the model considered here. If it is clearly established that the fluctuations do not arise from mechanical causes, then it appears that it will be necessary to propose a markedly different model for the reaction than that which has been examined in this paper.

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