Exothermic Gas Absorption with Chemical Reaction

The film theory for gas absorption with chemical reaction has been extended to take into account the release of heat due to solution and reaction. The analysis is applied to the industrially significant sulfur trioxide-dodecylbenzene system, and large increases in interface temperature are predicted during absorption. The enhancement factor behavior is correspondingly complex owing to the interaction of solubility reduction and rate constant enlargement. Some initial experimental measurements with the laminar jet technique confirm the need for and the basic soundness of the theory.

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SCOPE

This study has used the film theory to evaluate the consequences of large heat effects during absorption and chemical reaction. This is important because in cases where the heat effects result in a significant temperature increase at the interface, the absorption rate behavior is influenced by the tendency to reduced solubility of the absorbing gas and the enlargement of the reaction rate constant for a finite activation energy. These two effects counteract one another and give rise to complex possibilities for enhancement factor behavior.

Early theoretical work (Danckwerts, 1951) suggested that these effects were never likely to be significant. However, subsequent experimental evidence (Chiang and Toor, 1964, Mann and Clegg, 1975) for the high solubility systems ammonia-water and chlorine-toluene showed conclusively that large interface temperature increases were present. A theoretical analysis based on the penetration theory (Clegg and Mann 1969) had previously indicated that high solubility gas-liquid systems were likely candidates for such behavior.

The direct sulfonation of organic liquids with potentially highly soluble sulfur trioxide is an important unit process in which localized interfacial thermal effects have not so far been considered. The rational design of direct sulfonation gas-liquid reactors requires that this be done. Since multiple reagent petroleum types of liquid feedstocks are often utilized in sulfonation, evaluation of microscale interfacial temperature profiles is also necessary to understand product distribution when competing reactions have differing activation energies. Thus, if discoloring by-product reactions are to be understood and thereby suppressed and controlled, the kinetic parameters must be evaluated with respect to a complete understanding of the effect of a high degree of solubility and exothermicity on interfacial temperature behavior.

CONCLUSIONS AND SIGNIFICANCE

A film theory has been developed to describe gas absorption and interfacial temperature behavior under very exothermic conditions when the assumptions of constant solubility and isothermal behavior at the interface do not hold. Since the depth of heat penetration is usually much greater than that of mass penetration, the heat fluxes due to solution and reaction can both be treated as interfacial heat fluxes. This simplification, together with a linearized solubility relationship, gives rise to analytical forms for the enhancement factor, and surface temperature rise under slow and fast reaction conditions. The theory is illustrated for the high solubility system sulfur trioxide-dodecylbenzene, and large increases in interface temperature and enhancement factors below unity are predicted, showing that the depression of interfacial solubility can greatly reduce the absorption potential under reacting conditions. Some experimental results obtained from the laminar jet technique are compared with theory for both the linearized and the exact nonlinear solubility relationships. Large interface temperature increases are experimentally observed. The results could be important for rational design of gas-liquid reactors for the industrially important direct sulfonation of organic liquids, particularly with reference to the suppression of by-product reactions.

The release of the heat of reaction and solution close to a gas-liquid interface is an inevitable accompaniment to the processes of gas dissolution, mass transfer, and chemical reaction. Early theoretical work (Danckwerts, 1951), whose considerations were directed towards the sparingly and slightly soluble gas-liquid systems, was based upon the penetration theory and concluded that thermal effects, though finite, were negligible in terms of affecting the interfacial solubility equilibrium relationship. However, predictions for the system ammonia-water (Chiang and Toor, 1964) confirmed that nonnegligible interfacial temperature increases were possible, even though reaction was absent. Subsequently, penetration theory predictions (Clegg and Mann, 1969) for the reacting system chlorine-toluene showed that large interface temperature increases were likely when exothermic reactions were present in high solubility systems. Under these conditions, neglect of the boundary condition coupling between solubility and interface temperature would lead to serious overestimates of the absorption rates. These predictions were reinforced by experiments (Mann and Clegg, 1975) which showed that an interface temperature increase of 30°K which occurred in an exposure time of 40 ms (appropriate to bubble reactors and packed-bed contactors) could be inferred from laminar jet measurements. More recent work, while extending the previous approaches, has concentrated on interactions (Verma and Delancey, 1975) and various forms of approximation solutions (Shah 1972, Bentwich 1975) without identifying the conditions under which heat release would be highly significant, both for absorption rate calculations and more importantly for selectivity when multiple reactions are present.

The present work was prompted by a recently published model of a thin film sulfur trioxide reactor (Johnson and Crynes, 1974), which is a configuration that has been proposed for controlling more closely the temperature of the liquid phase reactant in order to improve the product blend and to suppress discoloring by-products in the direct sulfonation of organic liquids. The reactor model assumed infinite mixing rates within the liquid film and concentrated upon the axial temperature development, particularly the hot spot temperature and its location. Any inferences based upon such a model could be expected to be inadequate, since temperature profiles into the liquid film could give rise to significant excess temperatures at the interface, where, under the customary fast reaction conditions, most of the heat is released and where most of the reaction takes place. This paper treats the heat release and dissolution problem assuming the film theory is applicable and temperature and concentration gradients can exist across the film. The film theory is much easier to apply in this situation than the previously widely used penetration theory, since it avoids the time dependent interfacial boundary conditions. Under the normal equivalence of the film and penetration/surface renewal theories, the simpler film theory solutions should be adequate for evaluation and design purposes for thin film, bubble, and trickle-bed reactors.

FILM THEORY FOR EXOTHERMIC GAS ABSORPTION

During gas adsorption, the equation describing diffusion and first-order reaction after dissolution at the interface is given by

$$D\frac{d^2C}{dx^2} = k(T)C \tag{1}$$

and the transfer of heat is described by

$$\alpha\frac{d^2T}{dx^2} = \frac{-\Delta H_R}{c_p}\,k(T)C \tag{2}$$

subject to the boundary conditions

$$\begin{gathered} C = C^*(T^*) \text{ and } T = T^* \text{ at } x = 0 \\ C = 0 \text{ at } x = x_M \text{ and } T = T_b \text{ at } x = x_H \end{gathered} \tag{3}$$

The first boundary condition reflects the fact that when heat release is significant, any increase in interface temperature will depress the equilibrium solubility of the transferring gas. This is taken to be a major factor together with the temperature sensitive rate constant $k(T)$. The effect of temperature on diffusivity, liquid phase density, specific heat, etc., as well as coupling through the Dufour and Soret effects, has been considered to be secondary in importance and not included in the analysis. The second boundary condition implies that the bulk liquid phase contains a negligible concentration of the absorbing gas, at least in comparison with the interfacial value. This is almost always the case for conventional gas-liquid contactors when a reaction is taking place.

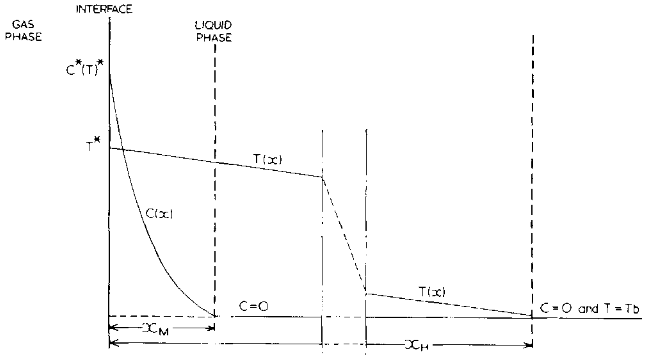

Fig. 1. Relative disposition of concentration and temperature profiles.

The boundary conditions of Equation (3) are not sufficient to solve Equations (1) and (2) because the interface concentration and temperature are not independent but are coupled through the solubility relationship. Further conditions that can be used to exactly specify four independent boundary conditions that solve the two second-order differential equations are the interfacial heat balance equation

$$\Delta H_s\left(-D\frac{dC}{dx}\bigg|_{x=0}\right) = -K\frac{dT}{dx}\bigg|_{x=0} \tag{4}$$

and the overall heat balance

$$\Delta H_s\left(-D\frac{dC}{dx}\bigg|_{x=0}\right) + \Delta H_R\left[-D\frac{dC}{dx}\bigg|_{x=0} - \left(-D\frac{dC}{dx}\bigg|_{x=x_M}\right)\right] = -K\frac{dT}{dx}\bigg|_{x=x_M} \tag{5}$$

Equations (1) and (2) are at first sight strongly coupled owing to the positional variation of the reaction rate constant with temperature. Their solutions with respect to the boundary conditions (3) and (4) or (5) are not possible, even semianalytically.

However, the physical reality of the situation provides for a greatly simpified method of solution due to the difference in magnitude of the mass and thermal diffusivities (commonly $\alpha = 100D$). In this event, the film thickness x_H over which temperature gradients exist is very much larger than the film thickness x_M over which concentration gradients are observed, and this is depicted in Figure 1. In other words, since $x_H >> x_m$, T^* is now considered to be constant across the mass transfer film, and this can be seen in Figure 1.

The differential equation for diffusion and reaction can now be written

$$D\frac{d^2C}{dx^2} = k(T^*)C \tag{6}$$

subject to

$$\begin{aligned} C &= C^*(T^*) \quad \text{at } x = 0 \\ C &= 0 \qquad\quad\; \text{at } x = x_M \end{aligned}$$

and now T^* is a lumped representation for the spatially dependent $T(x)$. The rate constant to use in the diffusion/reaction equation is therefore reasonably evaluated at the interfacial temperatureT^*. This interface temperature value is governed by the heat released due to solution and reaction, which can now both be considered to be interfacial heat fluxes within the framework describing heat transfer. The result is that $T(x)$, while being approximately constant over the distance x_M, must be linear over the distance x_H; therefore T^* is defined by

$$\frac{K}{x_H}(T^* - T_b) = \Delta H_s\left(-D\frac{dC}{dx}\bigg|_{x=0}\right) + \Delta H_R\left[-D\frac{dC}{dx}\bigg|_{x=0} - \left(-D\frac{dC}{dx}\bigg|_{x=x_M}\right)\right] \quad (7)$$

Equation (6) has the well-known analytical solution involving hyperbolic cosines, and the result in terms of an enhancement factor is given by

$$E = \frac{C^*(T^*)\sqrt{M'}}{C^*(T_b)\tanh\sqrt{M'}} \quad (8)$$

where

$$M' = Dk(T^*)/k_L^2 \quad (9)$$

Here E is defined relative to physical absorption if heat effects are completely ignored. Thus

$$E = \frac{\text{Absorption rate with reaction and heat effects}}{\text{Absorption rate for physical absorption with zero heat of solution}}$$

The enhancement factor defined by Equation (8) has two components. The term $\sqrt{M'}/\tanh\sqrt{M'}$ represents the improvement in absorption rate due to reaction. The term $C^*(T^*)/C^*(T_b)$ represents the reduction in available driving force due to heat release depressing the interfacial solubility.

Under fast reaction conditions, when $\tanh\sqrt{M'} \rightarrow 1.0$, all of the absorbing gas reacts within the mass transfer film, and in Equation (7) $dC/dx|_{x=x_M} \rightarrow 0$, so that this equation may be rewritten

$$h_L(T^* - T_b) = (\Delta H_R + \Delta H_s)C^*(T^*)\sqrt{Dk(T^*)} \quad (10)$$

where the liquid phase heat transfer coefficient is given by $h_L = K/x_H$

Therefore, the implicit relationship for the elevation of the interface temperature due to the release of heat of solution and reaction is obtained from

$$T^* = T_b + (\Delta H_R + \Delta H_s)C^*(T^*)\sqrt{Dk(T^*)}/h_L \quad (11)$$

In the absence of any reaction, that is, under physical absorption conditions, $\Delta H_R = 0$ and $\tanh\sqrt{M'} \rightarrow \sqrt{M'}$, resulting in

$$T^* = T_b + \Delta H_s C^*(T^*)k_L/h_L \quad (12)$$

Employment of a linear solubility relationship from

$$C^*(T^*) = C^*(T_b) - \mu_s(T^* - T_b) \quad (13)$$

makes Equation (12) now explicit in T^* so that

$$T^* = T_b + \frac{C^*(T_b)}{\mu_s + \dfrac{1}{\Delta H_s}\dfrac{h_L}{k_L}} \quad (14)$$

More important than this for gas absorption is the consequent reduction in the enhancement factor due to the depression of the interfacial solubility which is given by

$$E = \frac{1}{1 + \mu_s\Delta H_s\dfrac{k_L}{h_L}} \quad (15)$$

On the other hand, in the presence of fast reaction, Equation (14) becomes

$$T^* = T_b + \frac{C^*(T_b')}{\mu_s + \dfrac{1}{\Delta H_R + \Delta H_s}\dfrac{1}{\sqrt{M'}}\dfrac{h_L}{k_L}} \quad (16)$$

and the reduction in C^* follows so that

$$\frac{C^*(T^*)}{C^*(T_b)} = 1 - \frac{\mu_s}{\mu_s + \dfrac{1}{\Delta H_R + \Delta H_s}\dfrac{1}{\sqrt{M'}}\dfrac{h_L}{k_L}} \quad (17)$$

Both Equations (16) and (17) are still implicit in T^* because $\sqrt{M'}$ contains $k(T^*)$. However, for a reaction with zero activation energy, $\sqrt{M'}$ is replaced by $\sqrt{M}$ (which uses the rate constant evaluated at T_b) and the T^* is then obtainable explicitly. The explicit relationship for the enhancement factor when $E_R = 0$ is therefore given by

$$E = \frac{\sqrt{M}}{1 + \mu_s(\Delta H_R + \Delta H_s)\sqrt{M}\,k_L/h_L} \quad (18)$$

From this equation, it is clear that as $\sqrt{M'}$ becomes very large (in other words for very fast reaction), the enhancement reaches the asymptotic value

$$E = \frac{1}{\mu_s(\Delta H_R + \Delta H_s)}\frac{h_L}{k_L} \quad (19)$$

This means that as the reaction is made even faster, in contrast to the isothermal behavior when it increases linearly with $\sqrt{M}$, the enhancement factor remains stubbornly at a constant value. This conclusion has been arrived at by considering that the increase in interfacial temperature does not accelerate the reaction rate constant. However, in the case of a finite or even large value for the activation energy, replacement of $\sqrt{M}$ by $\sqrt{M'}$ which contains the value of $k(T^*)$ rather than $k(T_b)$ in Equation (18) gives rise to the same ultimate value for E. In fact, since $\sqrt{M'} > \sqrt{M}$, the asymptote of Equation (19) must be reached at smaller values of the corresponding equivalent value of $\sqrt{M}$.

The expression for the ratio of the enhancement factor at large $\sqrt{M}$ to the initial value for solely physical absorption is obtained from Equations (15) and (19) and by suitable rearrangement is given by

$$\frac{E\ (\text{fast reaction})}{E\ (\text{physical absorption})} = 1 + \frac{1 - \mu_s\Delta H_R\dfrac{k_L}{h_L}}{\mu_s(\Delta H_R + \Delta H_s)\dfrac{k_L}{h_L}} \quad (20)$$

From this equation, it can be seen that the advent of reaction can result in an ultimate increase or decrease from the initial (already depressed) value, depending upon whether $\mu_s\Delta H_R k_L/h_L$ is greater or less than unity. For large values of μ_s appropriate to high solubility systems and for large heats of reaction, the reaction can be expected to decrease the absorption potential. Indeed, reference to the enhancment factor is something of a misnomer in this situation, because under these conditions the reaction can be said to hinder the absorption process, whereas it is held by conventional interpretation to al-

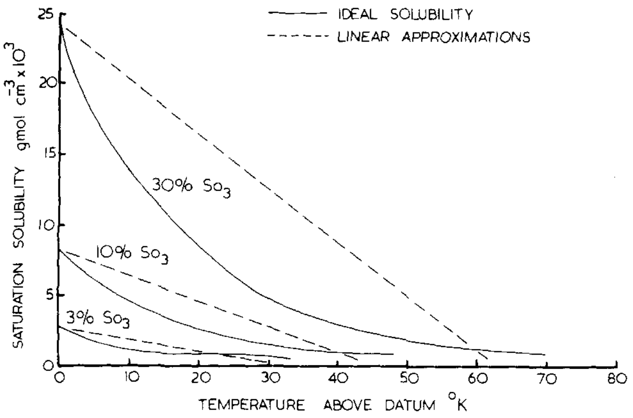

Fig. 2. Theoretical ideal solubility and linear approximations.

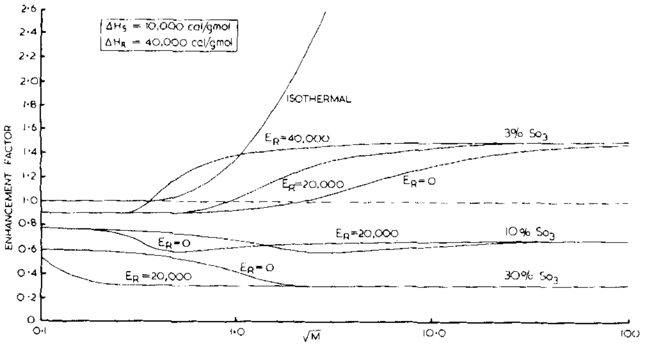

Fig. 3. Enhancement factor predictions from linearized solubility.

ways improve it. In the special instance when $\mu_S \Delta H_R \, k_L/h_L = 1$, the asymptotic enhancement factor at large $\sqrt{M}$ is unchanged from its initial value in the absence of reaction.

Thus, the confines of the overall behavior under slow reaction conditions ($\sqrt{M} \rightarrow 0$) and beyond the fast reaction regime ($\sqrt{M} > 5$) can be deduced analytically and explicitly. Intermediate ranges of reaction velocity can be solved for implicitly by using the appropriate expression for $dC/dx|_{x=x_M}$ in Equation (7) and the values for tanh $\sqrt{M'}$ between zero and one in Equation (8) (Moyes, 1976).

APPLICATION OF THE THEORY TO SULFUR TRIOXIDE-DODECYLBENZENE

The direct sulfonation of dodecylbenzene (DDB) using sulfur trioxide carried in a stream of dry nitrogen is an important gas-liquid reaction in the detergent industry. The reaction is certainly exothermic, and because of the high condensing temperature of sulfur trioxide, there are grounds for believing that the solubility level of sulfur trioxide in organic liquids is such that these systems might result in some of the largest conceivable increases in interfacial temperature and thus represent the upper limiting cases of exothermic gas-liquid behavior. In addition to this, by-product reactions perhaps involving discoloration of the main liquid product may be more temperature sensitive than the main sulfonation reactions, and in this event the occurrence of localized excess interface temperatures may have serious consequences for product quality.

Previous studies have indicated the importance of solubility level as a factor in determining the magnitude of any thermal effects. It is difficult, if not impossible, to experimentally determine the solubility of sulfur trioxide in DDB because the reaction is extremely fast, and a previous technique (Mann and Clegg, 1975) involving measurements at very low temperatures (when reaction is very slow) cannot be applied here as the gas has a relatively high condensing temperature. The use of a theoretical ideal solubility determined from an application of Raoult's law is the next best approach, and in many instances departures from ideality can be expected to be relatively small. Figure 2 shows the estimated solubility of sulfur trioxide in DDB (Moyes, 1976) for gas phase concentrations of 3, 10, and 30% of sulfur trioxide in nitrogen. These curves show the highly curved hyperbolic shape associated with the dependence of the log of the solubility on reciprocal absolute temperature. The equivalent linearized relationships that have been applied to the theory are also shown in Figure 2.

The predictions from the linear solubility relationships giving the enhancement factor as a function of the diffusion/reaction parameter $\sqrt{M}$ are presented in Figure 3. The asymptotes for slow and fast reaction can be clearly seen in Figure 3. The asymptotes for slow reaction are predicted from Equation (15) and for fast reaction from Equation (19). Intermediate reaction velocity cases were obtained implicitly (Moyes, 1976) via Equations (7) and (8) without making the assumption that $dC/dx|_{x=x_M}$ is zero. At the 3% level in the gas phase for physical absorption and under slow reaction conditions, the reduced interfacial solubility causes E to be attenuated from unity to 0.9. As the reaction is speeded up, E reaches an asymptotic value of about 1.5, but this ultimate unchanging value is greatly below that expected from a naive application of the isothermal theory. Thus, at $\sqrt{M} = 100$, neglecting heat release would imply an enhancement factor of 100, whereas in fact it will be only 1.5 which represents a dramatic sixtyfold reduction in absorption capability. Between the asymptotes for E there exists a region where the behavior is sensitive to the value of the activation energy E_R. Thus, at the 3% level $E_R = 40\,000$ cal/gmole results in an improvement over the isothermal case, but this is only sustained temporarily over a restricted range of $\sqrt{M}$. At the 20 000 cal/gmole level, the initial acceleration of E is insufficient to reach the values of the isothermal case.

For a gas phase containing 10% of sulfur trioxide E is initially depressed below 0.8, and the ultimate asymptote is 0.66. In cases of this type, where the ultimate value is below the initial value, E passes through a minimum at intermediate reaction velocities which in this case is 0.58. This minimum is independent of the value of E_R. It is significant that now larger values of the activation energy cannot improve the absorption performance, but on the contrary they intensify the hinderance. In this situation, it can be imagined that the balance of E lies with solubility reduction rather than with rate constant enlargement due to temperature rise. An increase in the temperature acceleration of the rate constant is more than cancelled out by the reduction in solubility.

For a gas phase containing 30% of sulfur trioxide, the initial fall in E is quite pronounced to 0.6, and it falls ultimately to around 0.3. Once again, a large activation energy only serves to accelerate the decline in the absorption capability. In passing from the initial to the final value, E goes through a minimum, though in this case it is very shallow and not easily detected in Figure 3. The related interface temperature increases above the datum of 298°K for 3, 10, and 30% sulfur trioxide are set out in Figure 4. In every case, the initial temperature increase undergoes a rapid further increase over a range of $\sqrt{M}$ values before reaching a value above which increased reaction speed does not give any further temperature increase. This is also the region in which E remains unchanged. At this condition, solubility reduction and absorption enhancement are exactly balanced against one another even if the reaction speed approaches infinity. The region of $\sqrt{M}$ over which a sharp increase in temperature occurs tends towards lower values of $\sqrt{M}$ as the proportion of sulfur trioxide in the gas phase increases. It is also noteworthy that there is a greater sensitivity to activation energy at higher concentrations of sulfur trioxide. However, the most striking feature of the theory is the very large surface temperature increases that are predicted. Even at the quite dilute level of 3% sulfur trioxide, a 25°K increase over the datum occurs at large $\sqrt{M}$. At the relatively high level (by industrial sulfonation standards) of 30%, a remarkable 60°K increase across the mass transfer film is predicted, and this compares with a close on 25°K increase for purely physical absorption.

COMPARISON OF THEORY AND EXPERIMENT

Good quality mass transfer data that can be reliably used to test theories on mass transfer are never easily obtained, and this is especially true for direct sulfonation systems since sulfur trioxide is difficult to handle. The authors have carried out a number of initial experiments using the laminar jet technique. This gives well-defined interfacial areas, and though better suited to provide data to test the penetration theory approach, it can also provide estimates of mass and heat transfer penetration depths for use in interpreting the film theory.

The laminar jet technique is now well developed and described in detail in several standard texts on gas-liquid reactions (for example, Danckwerts, 1970). Experiments were carried out running a laminar jet of DDB nominally 3 mm in diameter through controlled atmospheres of sulfur trioxide in nitrogen, produced by bubbling nitrogen through liquid stabilized sulfur trioxide (sulfan). Jet inlet and outlet temperatures were recorded on tenth degree thermometers, and bulk mixed temperature increases as high as 5°K were recorded for the highest concentration of 22.4% sulfur trioxide. These bulk mixed temperature increases due to absorption and reaction in the jet were interpreted using a depth of penetration for heat transfer evaluated from the penetration theory. Point interface temperatures at the entry of the jet into the receiver can then be inferred by relating the bulk mixed temperature increase, the temperature profile, and the corresponding integral peripheral heat accumulation (Mann and Clegg, 1975; Moyes, 1976). It has been assumed that the film theory applies to both heat and mass diffusion, and therefore the value of h_L is determined from

$$\frac{k_L}{h_L} = \sqrt{\frac{D}{K}} \tag{21}$$

The corresponding enhancement factors were determined by analyzing samples of the liquid stream after absorption and reaction in the jet for sulfonic acids by titration with $M/10$ caustic soda, and using the estimated datum solubility as given in Figure 2. This approach assumes that the absorbed sulfur trioxide primarily reacts to sulfonic acids. Though reaction to form sulfones may also occur, it is usually minor. A purple discoloration which slowly turned brown on prolonged standing of sealed samples was also observed. The intensity of the discoloration increased with increasing concentration of sulfur trioxide in the gas phase, though whether this is related to sulfone formation or some other by-product has not yet been determined.

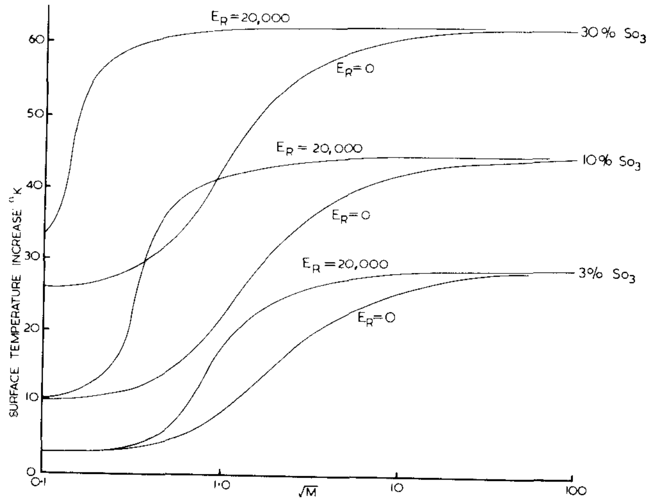

Fig. 4. Interface temperature predictions from linearized solubility.

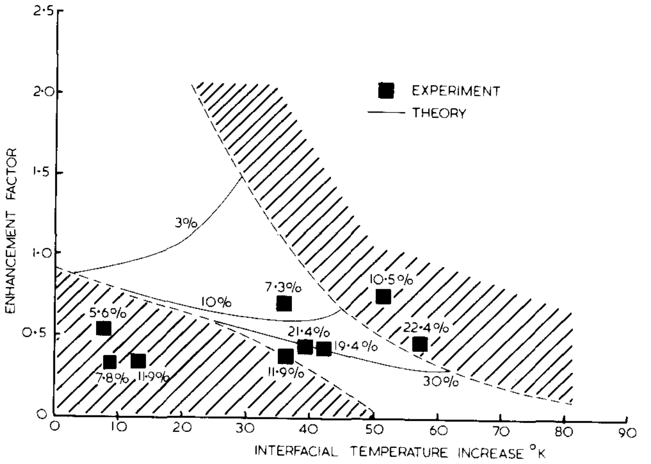

Fig. 5. Comparison of linearized theory and experiment.

Figure 5 shows the experimental results plotted on an enhancement factor-surface temperature plot. This kind of plot has to be employed to test the experiments, since the values of M and E_R are not known. The upper shaded region in Figure 5 is demarcated by the line of infinite reaction speed, that is, for $\sqrt{M} \rightarrow \infty$. At a given gas composition it is quantitatively determined by the upper asymptotes of E and T^* presented in Figures 3 and 4. Since $\sqrt{M}$ can never be greater than infinity, the shaded region cannot be entered. In a similar fashion, the lower shaded region in Figure 5 is demarcated by the line of zero reaction speed, that is, for $M = 0$. At a given gas composition it is quantitatively determined by the lower asymptotes of E and T^* presented in Figures 3 and 4. Though the correspondence between the experimental results and the theory is not complete, two aspects are confirmed by these results. Firstly, high temperatures appear to develop at the surface of the jet, and they are of the same order as those predicted from first principles assuming that the sulfur trioxide dissolves to form ideal solutions. Secondly, the experimental enhancement factors range from 0.4 to 0.7, confirming the theoretical idea that the heat release will depress the absorption potential in the high solubility sulfur trioxide-organic liquid systems resulting in enhancement factors lower than one.

A further aspect of the experiments concerns the validity of the linearized approximation. The upper shaded region in Figure 5 demarcates the higher limit of temperature increases predicted from the linear solubility relationships. Inspection of Fig. 2 in this respect shows that though the linear approximation is never very exact, it does become

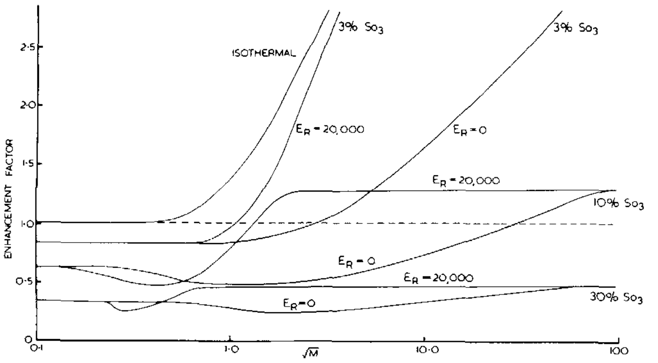

Fig. 6. Enhancement factor predictions from exact solubility.

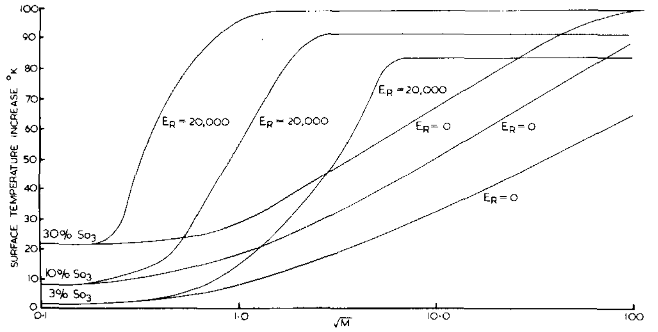

Fig. 7. Interface temperature predictions from exact solubility.

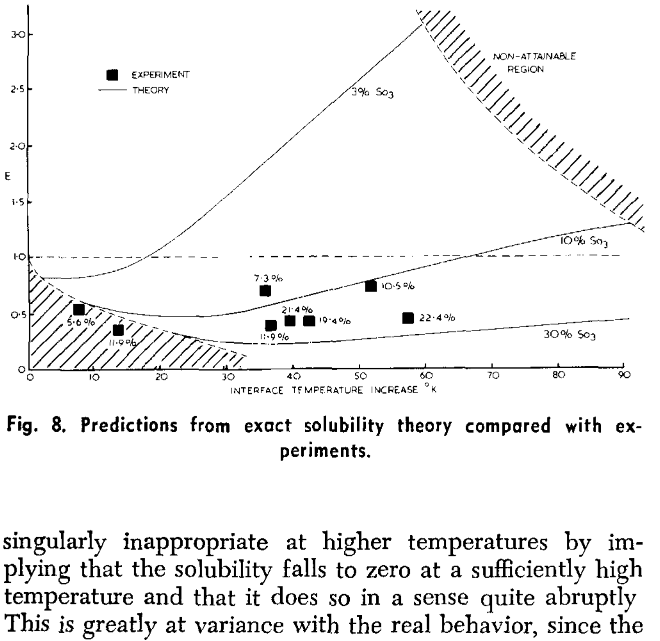

Fig. 8. Predictions from exact solubility theory compared with experiments.

singularly inappropriate at higher temperatures by implying that the solubility falls to zero at a sufficiently high temperature and that it does so in a sense quite abruptly This is greatly at variance with the real behavior, since the rate at which the solubility reduces with increasing temperature becomes very slow in all cases at higher temperatures. Thus, though the linearization (over a range) can be considered adequate as far as the point where the linearization crosses the curve, thereafter it is a very poor approximation. This point applies to the experimental results which indicate some interface temperatures higher than could possibly be predicted by the particular linearizations adopted to illustrate the linearized theory.

Solution of the film theory problem with the exact nonlinear solubility relationship by computation is quite elementary. The great disadvantage of the approach is that the character of the behavior cannot so easily be analytically deduced. The linearized approach is thus seen to be appropriate for preliminary evaluation of the likely magnitude of thermal effects from the relevant basic physicochemical data. Thereafter, if the effects are shown to be large, a specific nonlinear analysis for the particular case can be undertaken.

Figure 6 shows the enhancement factor behavior for the exact nonlinear solubility relationship. It can easily be deduced that the exact solubility relationship will give rise to lower values of the enhancement factor for solution without reaction (or at small $\sqrt{M}$ values), and that for large $\sqrt{M}$ the predicted values will be greater when compared to linearization (over a range). This is born out by the results presented in Figure 6. The divergence of the linear and nonlinear approaches is large for 3% sulfur trioxide, and the asymptotic value for E is not reached even at $\sqrt{M} = 100$. On the other hand, it is significant that the same kind of asymptotic behavior is exhibited and appears on Figure 6 for the higher 10 and 30% concentrations of sulfur trioxide. The intermediate behavior as the activation energy varies is quite similar to that observed for the linearized method.

Concerning the corresponding interface temperature predictions, because the solubility declines very slowly at the higher temperatures (rather than falling to zero), much greater interface temperatures become possible, as Figure 7 shows. At 30% sulfur trioxide, an upper interface increase of nearly 100°K is predicted, which is much higher than the 60°K of the linearized approach. This applies at all concentration levels, and the higher temperatures are all associated with greater enhancement factors.

The result of applying the exact solubility relationship is to produce a closer correspondence between the experimental observations and the film theory predictions. This can be clearly seen from Figure 8. Though the experimental results are somewhat sparse and open to further interpretation (concerning the values of $\sqrt{M}$ and E_R for the sulfur trioxide-DDB system), they indicate the necessity for a theoretical framework to describe highly exothermic gas absorption and reaction.

CONCLUSIONS

For gas absorption and reaction which is so exothermic that the assumption of constant interfacial temperature does not hold, using a linear solubility/temperature relationship, the film theory can be applied to predict analytically the enhancement factor and surface temperature increase under slow and fast reaction conditions. Severe reductions in enhancement factor in conjunction with large surface temperature increases up to 100°K are predicted using data applicable to the direct sulfonation of dodecylbenzene with sulfur trioxide. Experimental measurements using a laminar jet technique have shown that high interface temperatures can be reached and that reductions in absorption rate below that for physical absorption can occur. The theory and experimental findings emphasize the need for further studies, particularly concerning the effect of high surface temperatures on by-product reactions.

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NOTATION

c^* = interface concentration of absorbing component
C = concentration of absorbing component

c_p = specific heat of liquid phase
D = diffusivity of absorbing component
E = enhancement factor
E_R = activation energy
h_L = liquid phase heat transfer coefficient
K = liquid phase thermal conductivity
$k(T)$ = first-order rate constant at temperature T
k_L = liquid phase mass transfer coefficient
M = group $\sqrt{k(T_b)D/k_L^2}$
M' = group $\sqrt{k(T^*)D/k_L^2}$
T^* = interface temperature
T = temperature
T_b = bulk liquid phase temperature
x = position within liquid film
x_H = thickness of mass transfer film
x_M = thickness of heat transfer film

Greek Letters

α = thermal diffusivity
ΔH_s = heat of solution
ΔH_R = heat of reaction
ρ = density of liquid phase
μ_s = slope of solubility-temperature relationship

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Mechanics of Nonisothermal Polymer Melt Spinning

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Spin line tension, diameter attenuation, and the onset of the draw resonance instability are determined for a viscoelastic polymer melt, taking into account the changes in physical properties resulting from cooling of the filament. The theory predicts the experimentally observed stabilization of very short and very long filaments.

SCOPE

Melt spinning is the process of continuously drawing an extruded polymer melt into a fiber. The influence of melt viscoelasticity on the mechanics and certain aspects of the stability of the process is now reasonably well understood for spinning under isothermal conditions, but prior analyses of spinning under conditions where heat transfer is important have not considered the elasticity of the melt. Neglect of elasticity can result in grossly inaccurate estimates of spin line tension, diameter attenuation rate, and stability.

This paper is an extension of our previous analyses of the mechanics and stability of melt spinning (Denn et al., 1975; Fisher and Denn, 1976) to include the effect of heat transfer between the filament and surroundings as well as melt elasticity. The analysis is restricted to a Maxwell model of fluid viscoelasticity which has a single relaxation time and deformation-rate independent viscosity and modulus. In general, only qualitative results can be expected, but the model appears to be adequate for some polymers, including polyethylene terephthalate of intermediate intrinsic viscosity.

CONCLUSIONS AND SIGNIFICANCE

The effect of cooling is to increase the initial rate of diameter attenuation of a viscoelastic filament. Cooling inhibits the onset of a processing instability known as draw resonance, and the interaction of cooling and viscoelasticity results in a stabilization at high Stanton number which cannot exist for an inelastic liquid. Generally, short spin lines will be stabilized by fluid elasticity and long spin lines by cooling.

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