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Interfacial Area Generation In Two-Phase Systems and Its Effect on Kinetics of Phase Transfer Catalyzed Reactions

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Abstract: Rigorous treatment of PTC reaction kinetics requires a knowledge of how the system is affected by changes in interfacial area generation since this variable strongly affects the rates of the transfer step. Here, a simple equation is derived for estimation of interfacial area generation in laminar-flow liquid-liquid systems. While derivation of this equation did not consider many of the sophisticated and relevant phenomena which affect interfacial area generation, particularly those which occur at higher stirring speeds, the equation is highly useful for mathematical simulation of PTC kinetics to determine expected apparent reaction rate - stirring rate profiles. The equation also indicates a reciprocal relationship between interfacial tension and the rates of PTC reactions for which the transfer step is rate controlling. Calculation results are shown to be consistent with reported experimental data.

Keywords: stirring, agitation, phase-transfer-catalysis, kinetics, interfacial tension, interfacial area

I. Introduction

Rigorous description of the kinetics of phase transfer catalysis requires use of a complex set of equations integrating all the chemical reaction steps involved in the process, as has been demonstrated by Liotta.[1] At least two general steps are involved, (1) *the transfer step*, where one reagent is moved from its normal phase to or through the phase boundary where it can contact the second reagent, and (2) *the reaction step* wherein the transferred reagent reacts with the second reagent of the process. For example, in two-phase reaction of aqueous acetate with organic-phase benzyl chloride, the transfer step includes, among other competing ionic reactions, transfer of acetate anion from the aqueous phase to the organic phase, while the reaction step occurs by displacement of transferred acetate on benzyl chloride in the organic phase. Each of these steps may involve several separate or additional reactions, each with its own kinetic description. With more complicated systems there may be more than two general steps, particularly with hydroxide ion reactions.

The kinetics of organic reactions conducted entirely within a single phase, such as homogeneous acetate displacement of benzyl chloride in appropriate organic solvents, has been extensively studied for many years, and are reasonably well understood. However, kinetics of the set of reactions called the *transfer step*, where the total interfacial area is known, have only been studied to a very small extent, although "flat interface" experiments,[2] and work by Sharma and co-workers [3] are notable exceptions. Assuming that acetate transfer occurs at the interface, then for acetate transfer to an organic phase with a quaternary cation catalyst,

$$(Q^+ Cl^-)_o + (OAc^-)_{aq} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (Q^+ OAc^-)_o + (Cl^-)_{aq} \qquad \text{(transfer step)}$$

$$\text{R-Cl} + (Q^+ OAc^-)_o \xrightarrow{k_2} \text{R-O-Ac} + (Q^+ Cl^-)_o \qquad \text{(reaction step)}$$

we may write the kinetic description of the *transfer step* for Q^+OAc^- formation as in Eq. 1

$$\frac{d[Q^+OAc^-]_o}{dt} = k_1\ [Q^+Cl^-]_o\ [OAc^-]_{aq}\ [InterfacialArea] - k_{-1}[Q^+OAc^-]_o\ [Cl^-]_{aq}\ [InterfacialArea] \qquad (1)$$

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Now we come face-to-face with a major problem: a need to know the extent of interfacial area in a particular reaction system. We need an equation to tell us how the interfacial area will vary with measurable experimental and physical properties of the reaction system, such as stirring speed and interfacial tension. Then we could use a mathematical simulation technique to calculate the whole range of PTC reaction kinetics. From this, we may more completely understand the kinetic behavior for all types of PTC processes, and especially those in which the transfer step rate is important. Thus our first problem is to obtain a suitable way to calculate interfacial area generation in two-phase liquid systems.

II. Generation of Interfacial Area in Two-Phase Liquid Systems

Some general reviews [4, 5, 6, 7] for methods of study of two-phase reactions have been published, although mostly without reference to measurement of interfacial area. Basic studies by chemical engineers, particularly by those of Vermeulen, Williams and Langois [8] and by Fernandes and Sharma [9], and by others.[10] have shown that interfacial area generation is dependent upon several factors including: interfacial tension, impeller speed, reactor and impeller diameters and shapes, densities of the liquids and liquid viscosities. Experimental results for interfacial area, usually given in terms of *specific interfacial area*, equal to the total liquid-liquid interfacial area in the reactor divided by the total volume of liquids, and represented the symbol a, have been correlated with the above factors in rather complex empirical equations. While we could use these empirical correlations to calculate PTC kinetics, it was decided here to attempt development of an equation based on chemical principles. The result of this development is a simple equation which appears to provide reasonably good results at low stirring speeds, less than ca. 500 rpm for laboratory reactors, but at higher stirring speeds it needs some corrective terms. The reasons for deviation of the equation from "ideal" behavior are discussed in a subsequent section ("More Sophisticated Physics and Models") and lead to some appreciation for the complexity of the empirical equations noted above. Even though the simple equation is not perfect, it is usable at present for simulation of PTC kinetics.

1. Simple Equation for Estimation of Interfacial Area at Equilibrium

Consider the splitting of a "mother" droplet of suspended liquid into two daughter droplets. The increase in interfacial energy of the newly created interfacial area of the daughter droplets must come from the kinetic energy of the mother droplet. Once splitting has occurred, the daughter droplets are re-accelerated by the swirling liquids to stirring velocity, after or during which, each of the daughter droplets can likewise undergo splitting.[a] This splitting process will occur again and again giving smaller and smaller droplets until an equilibrium is reached wherein the rate of droplet coalescence is equal to the rate of droplet splitting. If we knew enough about the rates of splitting and coalescence we could use these rates to predict equilibrium droplet sizes. However, knowledge about these rates, or even the relevant parameters, appears to be almost completely absent from the scientific literature. Therefore, we must use an approach based on limiting droplet kinetic energy to estimate equilibrium. We start by asking the question "At a given stirring speed, what is the smallest size of mother droplet having just enough kinetic energy to split into two equal-sized daughter droplets?" (Unequal sized droplets are discussed later.)

Assuming a liquid-full (to avoid air bubbles and vortices) cylindrical reactor with a stirring blade reaching almost to the reactor wall, consider a single thin cylindrical shell of liquids as illustrated in Fig. 1. Within this shell of turning liquids consider a spherical mother droplet dispersed in the continuous liquid. Assume the mother droplet has a radius r_m cm, a specific gravity of ρ, the droplet is located at a distance x cm from the reactor center, and the droplet is turning with the liquid flow at a rate of ω revolutions per second in a

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[a] The precise mechanisms leading to splitting of a droplet of dispersed liquid are unknown, but logically one would expect that collisions of a droplet with other droplets, with solid surfaces, and with sections of the continuous liquid phase would be a primary cause of splitting. Additionally, splitting may come from interactions with turbulent eddy currents, and importantly, splitting may result from simple spinning of the droplet at sufficient rates to cause it to deform first to an ellipsoidal shape, then to continue deformation until it splits into two smaller equal-sized droplets.

circular path.

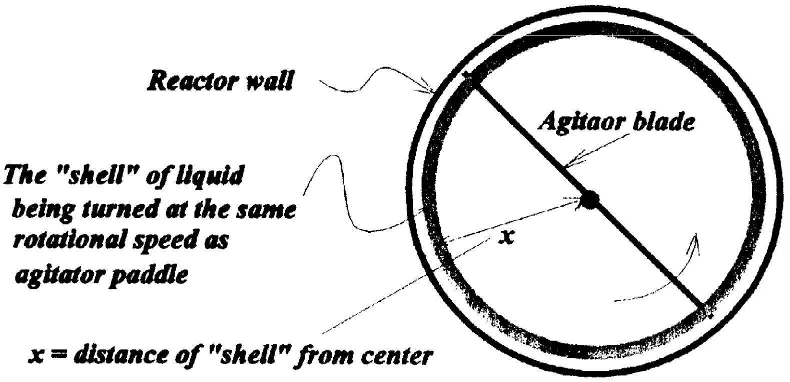

Figure 1: Schematic of reactor full with two immiscible liquids, turning at velocity of ω rev./sec. A cylindrical shell of liquid is considered for calculation.

Then, the translational kinetic energy (TKE) of the mother droplet in the shell is given by Eq. 2:

$$TKE = \frac{1}{2} m v^2 = \frac{1}{2} [\frac{4}{3} \rho \pi r_m^3] [\omega x]^2 \quad ergs \qquad (2)$$

Also, we can expect the droplet to be spinning, and therefore have spinning kinetic energy (SKE). The SKE of a sphere is calculated by integration of the kinetic energy of small volumes of the sphere over the whole, with the result, where ξ = droplet spin rate, rotations/second, given in Eq. 3:

$$SKE = \frac{4}{15} \rho \pi \xi^2 r_m^5 \quad ergs \qquad (3)$$

If we assume that the droplet must roll along the wall of the reactor (or the "wall" layer of the adjacent liquid shell) such that the velocity of the droplet sphere at its perimeter equals the linear velocity of the liquid in which it is moving, due to shear on the droplet, then spin rate may be related to liquid velocity as $\xi r_m = \omega x$. Substitution for ξ in Eq. 3 gives Eq. 4, which allows us to estimate SKE:

$$SKE = \frac{4}{15} \rho \pi r_m^3 \omega^2 x^2 \quad ergs \qquad (4)$$

Interfacial energy change. Since we have assumed that the mother droplet is split into two equal-sized daughter droplets, we can calculate the radius of the daughter droplets, $r_d = r_m / 2^{1/3}$, and this can be used to calculate the new interfacial area generated by the splitting. From this newly generated area and the interfacial tension, γ, the interfacial energy (ΔSE) required to form the two daughter droplets is given by Eq. 5:

$$\Delta SE = 4 (2^{1/3} - 1) \pi r_m^2 \gamma \quad ergs \qquad (5)$$

Finally, by combining the two kinetic energy terms, TKE and SKE, and equating them with the interfacial energy term, ΔSE, we can solve for the radius of the daughter droplets, $\mathbf{r_d}$, Eq. 6:

$$r_d = \frac{\frac{30}{7}\,(2^{1/3} - 1)\, n\, \gamma}{\rho\, \omega^2\, x^2} \quad cm, \qquad n = \frac{1}{2^{1/3}} \tag{6}$$

This simple equation, which contains no adjustable constants, allows one to estimate the equilibrium size of the smallest (equal-sized) droplets of a liquid formed at a particular distance out from the center of the reactor, given the values of stirring rate, suspended liquid density, and interfacial tension.

To proceed further we need to take into consideration that many sizes of droplets will probably be formed during splitting. To do this we could use the same kind of equations as Eq. 6, assuming that the total energy input available for interfacial area generation to the system remains constant, to compute the limiting size of *unequal-size* daughter droplet formation, by numerically specifying the volume fraction, **f**, of the mother droplet which goes to one daughter droplet with (1 - f) of the original mother droplet volume going to the other daughter droplet. This produces a series of equations, identical in form to Eq. 6, but with different values for the numerical constant ***n***. We might also consider variations in the amount of energy input available for interfacial area generation, by varying the exponent in the term $(2^{1/3}-1)$, all of which leads to a very large number of equations which must be solved simultaneously.

This author approached the estimation of droplet size distribution by assuming that a limiting constant amount of energy was available for interfacial area generation, i.e., that which is defined by equal-size droplet splitting, as in Eq. 5, and therefore retention of the term $(2^{1/3}-1)$. Further it is assumed that droplet sizes formed at equilibrium will have a distribution which is approximated by Boltzmann statistics. That is, the energy level represented in Eq. 5 for equal-size droplets is assumed to be the total energy available for splitting, but it must be distributed among all possible nonequal-size splittings according to splitting-energy required. Thus, for a given size of mother droplet, one can calculate the amount of interfacial energy, δe, required to split the mother droplet into two unequal-sized daughter droplets, by specifying what fraction, f, of the mother droplet volume goes to one of the daughter droplets. Then it is assumed that the probability, of the split to that value of f, relative to all other values of f between 0 and 0.5, is proportional to [$\exp(-\delta e)$.] Normalizing these values gives the assumed droplet-size distribution. When this kind of calculation was made by this author for 1000 values of f between 0 and 0.5, it was found that ***n*** in Eq. 6 should be replaced by the number 1/2, as in Eq.7, to better approximate the average size of droplet formed:

$$r_{avg} = \frac{\frac{30}{7}\,(2^{1/3} - 1)\,(\frac{1}{2})\,\gamma}{\rho\, \omega^2\, x^2} \quad cm \tag{7}$$

To determine the validity of Eq. 7, it is necessary to have experimental data which approximates a thin shell of liquid in a cylindrical reactor. In fact, the experimental study conducted by Vermeulen, Williams and Langois[8] was done in an apparatus quite similar to that outlined in Figure 1. Inserting the dimensions, interfacial tensions, and stirring rate data as reported by these workers into Eq. 7 allows one to calculate the average droplet radius, as shown by the continuous curves in Fig. 2 , and compare these with the experimental points reported by those workers. Considering the assumptions involved in Eq. 7, especially considering that Eq. 7 was derived with no adjustable constants, the match between predicted values and experimental results is remarkably good, with an average error of ± 23 percent.

Calculation of Specific Interfacial Area for Reactor: To arrive at an equation useful for PTC kinetics we need to calculate the specific interfacial area, ***a***, for a given reaction system. Assuming a liquid-full cylindrical reactor of radius L, and height 2 L, where all the liquid is turning at the same rotational speed, we assume that Eq. 7 describes the average droplet radius in a thin liquid cylindrical shell. Then integration over all the shells from the center of the reactor to the wall gives the total liquid-liquid interfacial area in the reactor. This, divided by total reactor volume gives ***a***. For a shell of liquids at a distance x cm from the center of the reactor, having a thickness of dx, and having a volume fraction, ϕ, of dispersed liquid in continuous liquid, then the volume of dispersed liquid, dV_d in the assumed cylindrical shell is given by Eq. 8:

$$dV_d = 2\ \pi\ (2L)\ \phi\ x\ dx \tag{8}$$

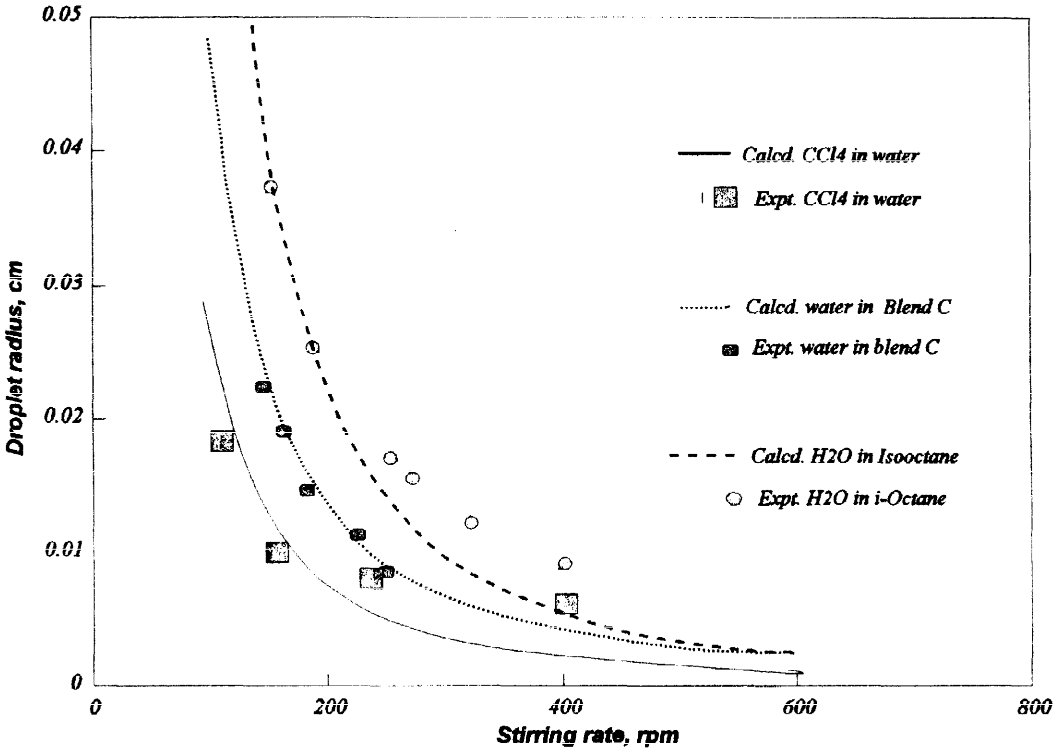

Figure 2: Droplet radii in liquid-liquid systems as a function of stirring speed. Comparison of predicted (lines) via Eq. 7 with experimental data (points). For CCl_4 in water, $\gamma = 39.9$ dynes/cm; $\rho = 1.579$ g/cc. For water in isooctane, $\gamma = 46.5$ dynes/cm; for water in Blend C (a blend of isooctane and CCl_4), $\rho = 0.998$ g/cc, $\gamma = 43$. For all runs x = 12 cm, $\phi = 0.2$. Data from ref. 8.

The total number of dispersed droplets in the cylindrical shell is calculated by dividing dV_d by the average droplet volume, and this number, multiplied by the average interfacial area per droplet, gives the total interfacial area in the thin shell, Eq. 9:

$$d(Area) = \frac{dV_d}{v_{droplet}}\ s_{droplet} = \frac{dV_d}{\frac{4}{3}\ \pi\ r_d^3}\ 4\ \pi\ r_d^2 = \frac{3\ dV_d}{r_d} \tag{9}$$

Combining, Eqs. 7 ,8, and 9 and integration of all shells between the center of the reactor and the wall, gives total interfacial area for the reactor, which divided by reactor volume, gives specific interfacial area, *a*, Eq. 10:

$$a = \frac{5.3862\ \rho\ \phi\ \omega^2\ L^2}{\gamma} \tag{10}$$

Experimentally[9] it has been shown that interfacial area generation is linearly proportional to ϕ, the volume fraction of dispersed liquid, in agreement with Eq. 10. Also, some references [10 f, g] have reported interfacial area generation to be proportional to the square of stirring speed, as indicated by Eq. 10, while others [10 d, h, i, j] found stirring speed exponents to range from 0.9 to 1.5. Reasons for this variation in exponent will be discussed below.

Equation 10 suggests that in a given apparatus the primary factors that will be of concern in the kinetics of phase transfer catalyzed reactions, as affected by total interfacial area, will be stirring speed, interfacial tension, concentration of suspended liquid (volume fraction), and density of the suspended phase. Equation 10 will be used in Part II to calculate interfacial areas as they are involved in the kinetics of PTC reactions.

2. Toward More Sophisticated Physics and Models in Interfacial Area Generation?

In the simple and idealized model for interfacial area generation discussed above several complicating factors were omitted. While these factors are not so important at low stirring speeds and with the simple apparatus pictured above, they become increasingly important and eventually dominate the physics at higher stirring speeds and with different apparatus. Currently, these factors are not well enough understood such that one can derive equations to describe them fully, but we can begin to qualitatively understand some of them.

Slippage Between Stirrer and Liquid: In the simple model it was assumed that liquid in the reactor moved at the same rotational speed as the stirring blade. However, we know that there must be slippage, i.e., incomplete mechanical coupling between the stirring blade and the liquid, and this slippage increases with rotational speed. Eventually, at high enough stirring speeds, cavitation occurs, and this causes so much slippage that mechanical coupling tends toward zero. Important conditions which influence cavitation include vapor pressure of the liquids, equipment geometry, and especially liquid velocity.[11]

Liquid Friction: The idea of liquid friction in a stirred reactor can be visualized by thinking of a small stirring paddle rotating in a very wide tank of liquid. Liquid around the stirrer will be moving, but will move more and more slowly as one moves out away from the agitator tip. If the reactor wall is far enough removed from the agitator blade the liquid at the wall may be essentially stationary. One may consider that the liquid in the gap space between the stirrer tip and the reactor wall consists of a series of thin liquid "shells" and that as these rotate the friction between an outer shell slows the liquid in the adjacent inner shell. As this occurs repeatedly between the reactor wall and the tip of the agitator, a velocity gradient in the gap between the wall and agitator tip is generated. This velocity gradient will be small for small gaps, except right at the wall surface where most workers believe that the thin layer of liquid adjacent to the wall is stationary.

Vertical velocity gradients between the bottom and top of the reactor may also result from liquid friction depending on the design of the stirring paddle or blade. If the blade is tall, i.e., extending the full height of the reactor, there should be no vertical velocity gradient. However, if as is normally the case, the stirrer is short compared to the height of the reactor, then liquid friction may induce vertical velocity gradients whose patterns will depend on whether the blade is at the top of the reactor, the bottom, or some intermediate position. For example, with a bottom-stirred reactor, the liquid at the top will lag the liquid at the bottom, causing a twisting action.

Reactor configuration: Equation 10 was derived on the basis that the extent of interfacial area generation and droplet size depended on the distance from the center of the cylindrical reactor. Clearly, if the reactor shape were different than cylindrical, or with height dimensions different than assumed for Eq. 10, the resulting equation for ***a*** will change. If the reactor were spherical or conical, as is typical of many flasks used in the laboratory, the equation would be different, but only to the extent of having different constants, not different variables. These constants may be determined by performing integrations appropriate to the shape of the reactor. Also, most commercial reactors have baffles, which increase shear and turbulence.

Reactor size: For a given liquid-liquid system, one might expect that as reactor size is increased, and its agitator and all related equipment are proportionally increased in size, and if the agitator velocity is adjusted to the same liquid velocity (tip speed), the specific interfacial area generated in two reactors would be identical. However, this is not the case. Specific interfacial area decreases as the reactor size is increased.[9] Chemical engineers have long recognized this unexpected behavior and have used the scale-up rule that *agitation power* per unit of liquid volume must be kept constant to achieve equal values of specific interfacial area. What is the cause of the decreased specific interfacial area with increasing radius?

One clear reason for decreasing interfacial area with reactor size, under the proportional assumptions defined above, is that if all the dimensions of the reactor and stirrer are increased in proportion to the reactor radius, then the gap between the stirrer tip and the reactor wall will increase in proportion with the reactor radius. As noted earlier, increasing the size of this gap increases the extent which liquid friction can slow the velocity of the liquid in this gap, compared to the rotational velocity of the stirrer. Since this gap mostly affects the outermost liquid, where the most interfacial area is likely to be generated, we can see that liquid friction in the gap will have a greater slowing action and to decrease interfacial area generation more in large-radius reactors than in smaller ones. On this basis we expect that specific interfacial area would vary with the reciprocal of reactor radius, as indeed appears to be the case when Fernandes and Sharma's data[9] are so plotted, as shown in Figure 3.

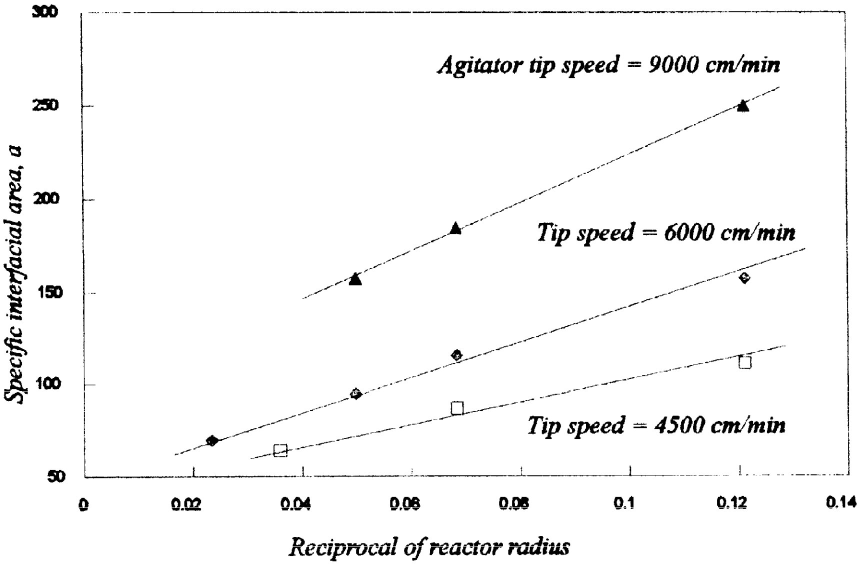

Figure 3: Variation of specific interfacial area generation with reciprocal of reactor radius. Data of ref.[9] using four-bladed paddle agitator; system of 2-ethylhexyl formate and 0.2 M NaOH solution.

Agitator size and shape: In accordance with the discussion above about liquid friction, it would be expected that agitators which extended out almost to the reactor wall would be the most efficient. However, experimental data of Fernandes and Sharma[9] suggest that for the ratio of impeller length to reactor diameter there is an optimum value, 0.5. This was explained as too much slippage at low ratios, and too much energy loss due to turbulence at high ratios. Even so, this optimum ratio may change with reactor size and shape.

Fernandes and Sharma[9] also examined the effect of agitator shape on interfacial area generation in a system of 2-ethylhexyl formate : 2 M NaOH, at constant agitator tip speed. For various agitator shapes under otherwise identical conditions they found the following values for specific interfacial areas (cm^2/cm^3) : six-bladed straight turbine, 135; six-bladed straight paddle, 103; six-bladed curved paddle, 98; four-bladed straight paddle, 95; four-bladed 45°inclined paddle, 90; four-bladed curved paddle 88; three-bladed propeller 65.

Mixing and centrifugal separation: In the derivation of Eq. 10 it was assumed that there was little mixing between the various regions of the reactor, either radially or vertically. Mixing certainly does occur to a greater or lesser extent and, in fact, many agitators are designed and chosen to facilitate mixing, rather than to generate interfacial area. Such mixing changes the distribution of droplet sizes within a given volume of liquid, and therefore would be expected to change the rates of droplet coalescence. However, since so little experimental data is actually available about coalescence rates, the extent to which mixing affects droplet size and interfacial area, compared to the other factors affecting size and area, is quite unknown.

Unless the two liquids of the heterogeneous mixture have approximately the same density, there will be some tendency for the droplets of dispersed liquid to move either toward the walls of the reactor or toward the center of the reactor because of centrifugal force. This tendency, dependent on the relative densities of the two liquids and the stirring speed, therefore exerts a centrifugal separation or concentration effect. Because of droplet velocity, this effect should increase interfacial area if suspended droplets are concentrated toward the walls (although counteracted to some degree by an expected increased coalescence rate due to increased concentration), or a decrease in interfacial area if suspended droplets are concentrated toward the center of the reactor (and even more decreased by increased coalescence rate.)

Turbulence: While increasing the flow rate of a homogeneous liquid through glass tube or pipe, Osburn Reynolds [12] observed that, on reaching a certain critical velocity, small visual discontinuities ("turbulence or eddy currents") appeared, and the apparent concentration and intensity of these discontintinuties increased on further increases in flow velocity. Liquid flow is called *streamline* or *laminar* below this critical velocity, and *turbulent* above this velocity. Reynolds found the critical velocity to be dependent on the pipe diameter, liquid viscosity, and liquid density, and through the use of the so-called *Reynolds Number*, one can approximately predict the fluid velocity where flow will change from streamline to turbulent. This on-set of turbulence in liquid flow is very important commercially, since turbulence requires substantially more pumping energy and higher pipe pressure ratings than in its absence. The theory, mathematics, and science of turbulence in flowing liquids has been extensively explored, and is painfully complex.[13]

Turbulence, as outlined in the previous paragraph, also occurs when a liquid is stirred in a reactor, and it also occurs when the reactor contains two immiscible liquids. With most liquids in a one- or two-liter flask, it is roughly estimated (based on Reynolds Number) that onset of turbulence occurs at stirring speeds of about 250-500 rpm. The important point about turbulence in a stirred reactor is that the energy required for turbulence formation is taken from the kinetic energy of the moving liquids, and is therefore not available for formation of interfacial area. At higher and higher stirring speeds above turbulence-onset a higher fraction of energy that would have gone to generating interfacial area will instead now be consumed by turbulence. This reduces the extent of interfacial area generation, compared to where non-turbulent conditions.

Some workers[10 b-e] have proposed that the eddy currents in turbulence are themselves mechanically responsible for at least a part of droplet splitting. That is, the eddy currents of continuous-phase liquid are believed to interact like tiny cyclones with droplets of dispersed liquid causing the dispersed droplets to break up into even smaller droplets. Most of the turbulence is initiated at the walls, at baffles, and at the agitator blade surfaces where a high level of shear exists between the liquid and solid surfaces. Further complicating the picture is the non-uniformity of liquid velocities in the reactor. Since the velocity of the liquid flow increases from near zero at the center of the reactor to a maximum near the reactor wall, the outer regions may be turbulent at high enough stirring speed, but in regions near the reactor center liquid flow may not be turbulent.

A More Sophisticated Equation?: From the factors outlined above, we can expect that in interfacial area generation, ***a*** will be proportional to the square of velocity at low speeds but will fall away from a simple velocity-squared curve as stirring speed is increased due to friction, turbulence and slippage. This kind of behavior was seen in the data of Vermeulen et al in Fig. 2, since experimental droplet diameters do not decrease as rapidly as expected at stirring speeds greater than about 300 rpm. Deviation from Eq. 10 is even more clearly seen in the results of Fernandes and Sharma[9] as in Fig. 4, where ***a*** falls away from a second order dependence on stirring rate at about 300 - 400 rpm, to a more-or-less linear dependence at 500-1500 rpm, then falling off even more at higher stirring speeds.

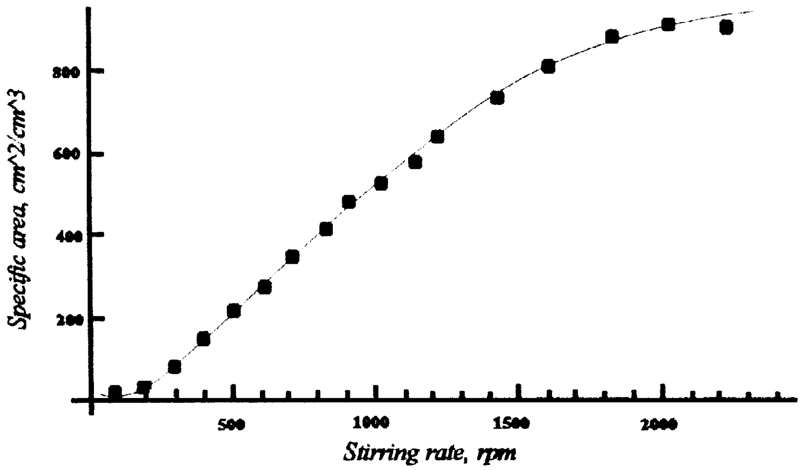

Figure 4: Specific interfacial area vs. stirring speed for n-octyl formate dispersed in 2 M NaOH. $\phi = 0.5$ Data from ref. 9.

We can go through the factors discussed above, and perhaps others, and for each we can probably find some physical or empirical equations to approximate the effect of each, and therefore could modify the simple equation, Eq. 10 to match a particular set of data. In general, however, this approach will require the use of one or more arbitrary or adjustable parameters, as has been done in most of the prior work on understanding and prediction of interfacial area generation.[10] While this level of sophistication is often desirable, it does not seem appropriate at the present time for PTC reactions because of the lack of theoretical understanding and too little experimental data. Since most PTC reactions are run at stirring speeds of 500 rpm or less, we are assuming, at least for the present time that Eq. 10, although imperfect, is adequate for the kinetic simulations next described.

III. Interfacial Area Generation and Phase Transfer Catalysis Kinetics

As outlined in the introduction, the kinetics of phase transfer catalysis minimally involve two steps, (1) a transfer step and (2) a reaction step. For the example of PTC acetate displacement on an alkyl chloride the differential equations 11 and 12 are assumed to describe the process kinetics:

$$\frac{d[Q^+OAc^-]_o}{dt} = k_1\,[Q^+Cl^-]_o\,[OAc^-]_{aq}\,[I] - k_{-1}[Q^+OAc^-]_o\,[Cl^-]_{aq}\,[I] \tag{11}$$

$$\frac{d\,(RCl)}{dt} = -\,k_2\,(RCl)\,(Q^+OAc^-)_o \tag{12}$$

In these equations, $[I]$ represents interfacial area. $[I]$ may be replaced by $a\ Vo$, where Vo is the total liquid volume in the reactor, and a is the specific interfacial area, calculated from Eq. 10. The mathematical simulation technique pioneered by Liotta[1] for numerical integration of the PTC kinetic equations, now with an added mathematical term to represent interfacial area, allows one to examine calculated kinetic behavior of PTC reactions such as acetate displacement at various stirring speeds. Responses of the kinetics, particularly to stirring speed and interfacial tension effects are important, and this mathematical procedure allows us to compare calculated behavior with experimental behavior.

1. Effect of Stirring Speed

The procedure used here was to select: (1) all the reaction parameters such as volumes, moles of reactants used, reactor size, etc, which are to be the same for all simulated kinetic experiments, (2) range of values for the rate constants k_1 and k_2, ignoring for the moment the value of k_{-1}, and (3) the range of stirring speeds that will be used for calculations. Using the computer software *Mathematica,* and a given pair of values of k_1 and k_2, at a given stirring speed, the concentration of reagents and products as a function of time was computed by numerical integration. From the calculated product concentrations after a short reaction time (1 to 5

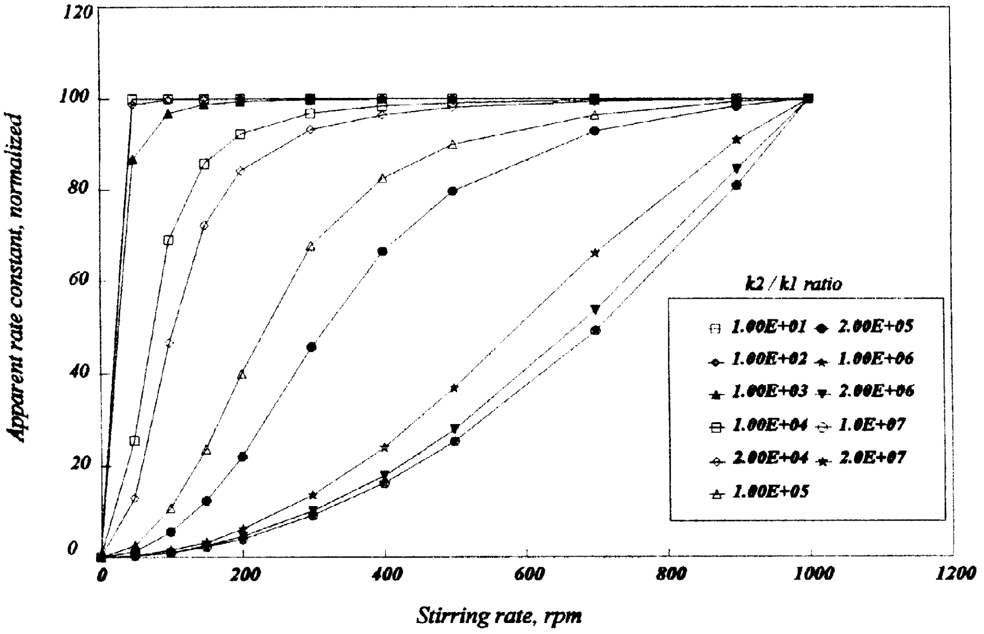

Figure 5: Calculated and normalized apparent rate constants, ka, vs. stirring rate for PTC Reactions at various k2 /k1 ratios. Data normalized to 100 for comparison.

minutes), an *apparent first order reaction rate constant,* k_a was calculated by the usual first-order kinetic equations. The reason for using apparent first-order rate constants is to allow comparison with literature-reported data, most always given as apparent first-order, or pseudo first-order, rate constants. After such computations over the whole range of stirring speeds of interest, usually at ten or more stirring speeds, the apparent rate constants as a function of stirring speed were plotted by *Mathematica* for each k_2/k_1 ratio. Combining the data of several such plots gives the family of curves shown in Figure 5. Note that in this figure and the next the values of k_a are normalized as a percentage or fraction of the maximum rate to allow convenient comparison of the curves.

The resulting curves all show the expected behavior. At low stirring speeds, the rate of the transfer step is always either the rate determining step, or at least is an important component of the overall rate, so apparent rates rise rapidly with increased stirring rates. At higher stirring speeds, for k_2/k_1 ratios less than ca. 10^5 the transfer step becomes faster and faster, until at some speed, the apparent rate no longer increases with increasing stirring speeds, but reaches a maximum level or plateau. At this point the rate of the whole process depends only on the reaction step rate, becoming independent of the rate of the transfer step, and therefore independent of stirring speed. At higher values of the k_2/k_1 ratio, i.e., greater than about 10^7, the reaction rate is so fast that any transferred reagent is virtually instantaneously consumed at the interface, so these reactions are clearly rate-limited by the rate of the transfer step. Such reactions with very high k_2/k_1 ratios would not show the plateau-effect commonly observed with lower values of this ratio, and apparent rates would continually increase with increasing stirring speed, at least within the speed restrictions of Eq. 10. A plot of experimental data for reactions of this type, at stirring speeds over 500 rpm, may appear to be more or less linear.

Comparison of curves with literature data: In Figure 6 are plotted a selection of normalized apparent-rate: stirring rate profiles for seven different phase transfer catalyzed reactions wherein the stirring speeds were mostly below 1000 rpm. (See ref.[14] for the sources of these data.) These experimental rate data show the same behavior pattern as illustrated for the calculated curves of Fig. 5. Even the somewhat complicated

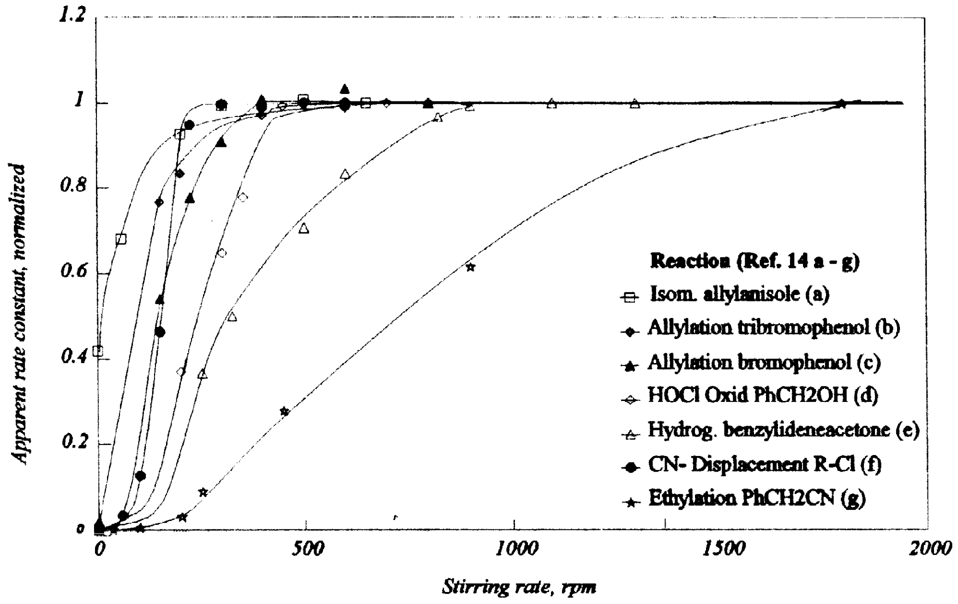

Figure 6: Experimental apparent rates -stirring rate profiles for seven PTC reactions.

alkylations with NaOH generally fit the expected patterns, although tending toward a plateau rather than curving upward, but in a stirring-rate region well beyond Eq. 10's capability.

A particularly interesting item in Fig. 6 is the 50-300 rpm section of the cyanide displacement curve. If the first four points of this curve are plotted in a log-log manner with stirring speed, the points fall reasonably well on a straight line with a slope of about 2, indicating for this region of this reaction the mass transfer rate, and therefore interfacial area, is proportional to the square of the stirring speed, in agreement with Eq. 10.

One other point of general interest is the question of how the rate constant of the reverse part of the mass transfer step, i.e., k_{-1} affects PTC kinetics. When k_{-1} is allowed to assume significant values then its effect on apparent rates can be calculated, as shown in Fig. 7. Here it is seen that increasing the reversibility of the mass transfer rate by increasing the k_{-1}/k_1 ratio does not significantly affect the general shape of the curve, but only lowers the overall apparent rate and it moves the point where the rate reaches a plateau back to lower stirring rates. The calculation procedure used above can be extended for use with all types of complicated phase transfer catalyzed reactions by including the appropriate differential equations in the numerical integration process. For example, the procedure was found to be useful for analysis of reactions which show autocatalysis or auto-inhibition (i.e. reactions with *in situ* generation of quaternary salts or gradual decomposition of quaternary salt catalysts.)

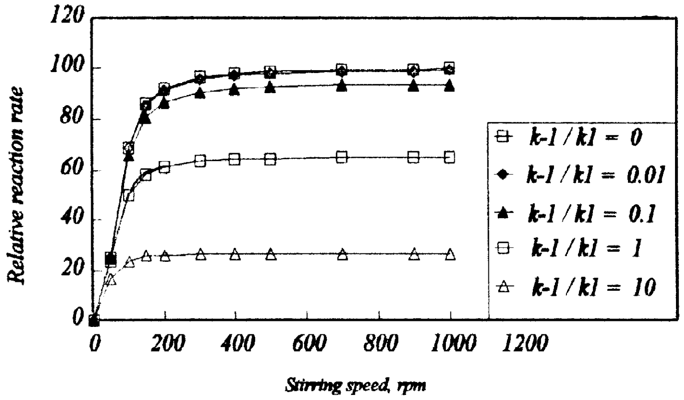

Figure 7: Effect of increasing k-1/k1 ratio on stirring profile
k2 / k1 = 1.0 E 4

This calculation procedure is not yet useful for liquid-liquid PTC reactions at high stirring speeds. Nor is it applicable to liquid-solid PTC reactions, where interfacial surface area is apparently controlled by mechanisms different than those discussed here. Experimentally, rates of liquid-solid PTC reactions, at least at high stirring rates,[15] seem to follow simple linear relationships with stirring speed,

2. Effect of Interfacial Tension

Interfacial tension, γ, is a significant variable in Eq. 10, like stirring speed, affecting the extent of interfacial area generation in liquid-liquid systems. Therefore, we expect that for reactions where the rate is primarily dependent on the rate of the transfer step, apparent rates will be reciprocally dependent on interfacial tension. The rates of reactions which are primarily dependent on the rate of the reaction step, and not the transfer step, will not be affected by interfacial tension.

Interfacial tension is itself dependent on several factors including, (1) the nature of the two liquid phases, the more nonpolar the organic phase, the higher is γ, (2) the presence of any material, including

stirring speed gives a near-linear plot, indicating that in this system the transfer step is rate-limiting.

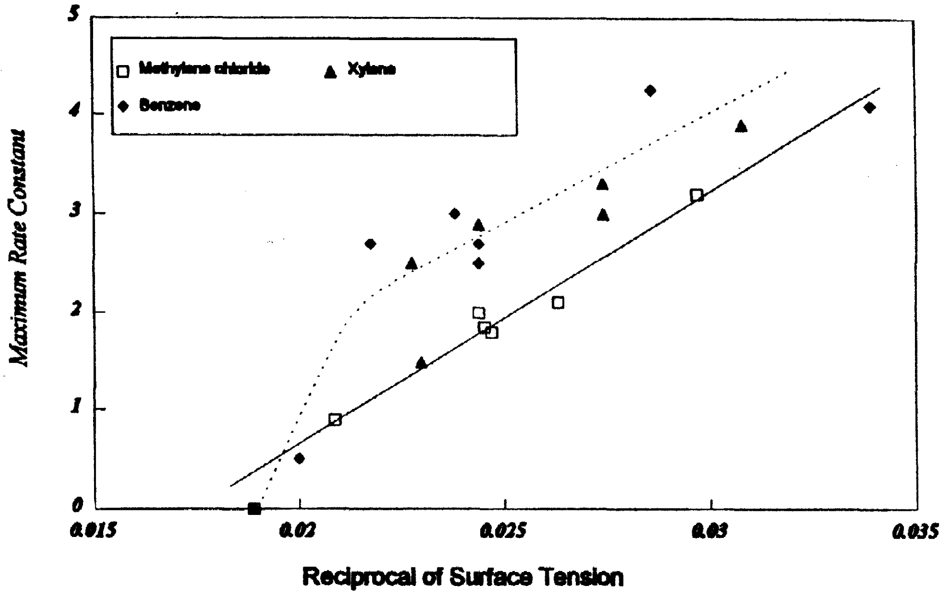

Figure 8: Reaction rate variation with interfacial tension in PTC ethylation of desoxybenzoin with 50% NaOH and various tetraalkylammonium salt catalysts. Data from Ref. 16.

References

1. Liotta, C. L., Chapter 3, p. 48, in *Phase Transfer Catalysis, Fundamentals, Applications, and Industrial Perspectives*, by Starks, C.M., Liotta., C.L., Halpern, M.., Chapman and Hall, New York, 1994.
2. (a) Yamashita, Haruo; Kunigita, Euchi, *Kagaku Kogaku Ronbunshu*, **1987**,13(6), 788-4.[CA108(23):204283] (b) Nakamura, H.; Asai, S.; Yamada, M., *Chem. Eng. Sci.* **1998**, 51(8), 1343-6 [CA 124.344032] (c) Sawarkar, Chhaya S.; Juvekar, Vi nay A., *Ind. Eng. Chem. Res.* **1996**, 35(8), 2581-2589.
3. Lele, S.S, Bhave, R.R, Sharma, M.M., *Chem. Eng. Sci.*, **1983**, **38**, 765.
4. Atherton, H., *Trans Ichem E.*,**1993** March, 71, Part A, 111.
5. Tavlarides, L.L., Stamatoudis, M., *Adv. Chem. Eng.*, **1981**,11, 199-266.
6. Hanna, G.J., Noble, R.C., *Chem. Revs*, **1985**., **85**, 583.
7. Cussler, E.L., *Chemtech*, **1986**, 422.
8. Vermeulen, T., Williams, G.M., Langlois, G.E., *Chem. Eng. Prog.*, **1955**, 51, 85F.
9. Fernandes, J.B., Sharma, M.M., *Chem. Eng. Sci.*,**1967**, 22, 1267.
10. (a) Lele, S.S., Bhave, R.R., Sharma, M.M., Chem. Eng. Sci., **1983** 38, 765; (b) Rodger,W.A., Trice, V.G., Jr., Rushton, J.H. *Chem. Eng. Progr.*, **1956**, 52, 515; **1952**, 48, 297; (c) Bohr, N., Wheeler, J.A., *Phys. Rev.*, **1939**, 56, 426; (d) Hinze, J. O., *AIChEJ*, **1955**, 1, 289 ; (e) Magnusson, K., *Chem. & Process Eng.*, **1954**, 35, 276; (f) Madden, A.J., Damerell, G.L., *AIChEJ*, **1962**, 8, 283; (g) Rushton, J.H., Nagata, S., Rooney, T.B., *AIChEJ*, **1964**, 10, 298; (h) Shinnar, R., Church, J.E., *Ind. Eng. Chem.*, **1960**, 52(3), 253; Sprow, *Chem. Eng. Sci.* **1967**, 22, 435 ; *AIChEJ* **1967**, 13, 995; (i) Kafarov,V.V., Babanov, B.M., *J. Appl. Chem. USSR*, **1959**, 37, 173; (j) Pavlushenko, I.S., Yanishevskii, A.V., *J. Appl. Chem. USSR*, **1959**, 32, 1529.
11. Sakiadis, B. C. , *Fluid and Particle Mechanics*, Perry's *Chemical Engineers' Handbook*, **1984**, Ed 6., p. 5-61.
12. See: Hammer, L., Silbar, M.L., *Science Digest*, **1984**,92, (5) 49 for a simplified review of turbulence.
13. (a) Bradbury, L.J.S., Durst, F., Launder, B.E., Schmidt, F.W., Whitelaw, J.H., *eds.*, *Turbulent Shear Flows*, Springer-Verlag Publ., New York, 1980; (b) Stanišić, M.M., *The Mathematical Theory of Turbulence*, Springer-Verlag, New York, 1988; (c) Cutter, J., *AIChEJ.*, **1966**, 12, 35.

14. (a) Neumann, R., Sasson, Y., *J. Org. Chem.*, **1984,** 49, 3448; (b) Wang, M.-L., Wang, H.M., *Ind. Eng. Chem.*, **1990,** 29, 522; (c) Wang, M.L., Yang, H.M. *J. Mol. Catal.*, **1990**, 62, 135; (d) Azran, J., Buchman, O., Amer, L., Blum, J., *J. Mol. Catal.*,**1986**, 34, 229; (e) Do, J.S., Chow, T.C., *Ind. Eng. Chem.*, **1990,** 29, 1095; (f) Starks, C.M., Owens, R.M., *J. Am.Chem. Soc.*, **1973**, 95, 3613 ; (g). Solaro, R., D'Antone, S., Chiellini, E. , *J. Org. Chem.*, **1980,** 45, 4719.

15. Pradhan, N.C., Sharma, M.M., *Ind. Eng. Chem.*, **1990,** 29, 1103; **1992**, 31, 1606.

16. Mason, D,. Magdassi, S., Sasson, Y., *J. Org. Chem.*,**1990,** 55, 2714.

17. The ability of some longer chain quaternary salts, including Aliquat 336, to lower interfacial tensions has been probed by Gupta and Patil, [Gupta, N.N., Patil, G.S., *Can. J. Chem. Eng.*, **1993,** 71, 802] and the ability of tetrabutylammonium chloride, bromide and iodide to lower interfacial tension between hexane and water has been reported by Tamaki .[Tamaki, K., *Bull. Chem. Soc. Japan*, **1967**, 40, 38.]

18. Asai, S., Nakamura, H., Tanabe, M., Sahamoto, K., *Ind. Eng. Chem.*, **1994, 33**, 1687.

19. Krishnakumar, V.K., Sharma, M.M., *Ind. Eng. Chem.*, **1965**, 24, 1297.