Mass Transfer During Drop Formation on the Nozzle: New Flow Expansion Model

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*An attempt was made to introduce a new approach for evaluating mass transfer during drop formation via definition of a parameter related to the extent of the convective mixing within the growing drop. For this purpose it was assumed that the entrance of the dispersed flow into the growing drop from the nozzle is analogous to the entrance of the flow from a smaller channel to a larger one. This transfer mechanism has been dubbed the "flow expansion." A global time-dependent Reynolds number of growing drop (Re_{gd}) was defined based on the equivalent diameter of growing drop as a length scale and also on a velocity scale, which is obtained using this flow expansion assumption. The results show that (Re_{gd}) has an important role on the mass transfer coefficient. The results of the model for prediction of instantaneous mass transfer coefficients and total cumulative mass transfer demonstrated relatively good agreements with experimental data. In some cases, however, for large nozzle diameter and relatively low nozzle velocity, i.e. in cases with large nozzle time scale ($T_N = R_N / U_N$), the flow expansion model showed some shortcomings. Subsequently, a modification called the transient flow expansion model was introduced which could improve the results of the previous model for large T_N cases. Comparison of the results of the transient flow expansion model with experimental data reported in the literature showed relatively good agreement for a wide range of operational conditions: nozzle diameter, nozzle velocity, final formation time and various liquid-liquid systems. The capabilities of the model were also evaluated in comparison with other well-known analytical (*surface stretch *and the* fresh surface elements*) and semi-empirical models, along with available experimental data. The comparison of the model with the previous incorporated convection/circulating models demonstrated a high potential for this new approach.* *AIChE J,* 52: 895–910, 2006
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Introduction

Liquid-liquid systems are important in many areas of engineering, physics, and chemistry. A few examples of current interests are liquid-liquid extraction equipments; emulsion technology; space applications in propulsion systems, life support and storage; oil-water mixtures in pipeline flow; extrusion of polymers; secondary oil recovery and interfacial tension measurements. Among these examples, liquid-liquid extraction is an important unit operation with considerable industrial applications. This process involves the separation of components of a homogeneous liquid by transferring them between

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contacting immiscible or partially miscible liquids. This technique is used as an energy-saving alternative to distillation in many industrial processes such as petrochemical, wastewater treatment, hydrometallurgical and oil refining industries. Large-scale production requires extraction columns with diameter of several meters and as a result volume of the order of several hundred cubic meters. Accordingly their design procedure can have a significant impact on the economical analysis. For this purpose sufficient knowledge about the hydrodynamics aspects and the interfacial mass-transfer rate are required for droplet formation, falling/rising, and coalescence stages.

Although there are extensive experimental, theoretical and numerical studies on dynamics of droplet formation in liquid-liquid systems, the evaluation of mass transfer during droplet formation is rather complex and there has been little research done on this subject.[1] The various mathematical models developed for this problem are generally based on a solution of the diffusion equation without allowance for circulation within the droplet. This can be the main reason for the poor prediction of these models in many cases for which internal convection has an important effect on the mass-transfer rate. Although a few improved models were developed in which convection and circulation terms have been considered[2, 3, 4] each of them has its shortcoming in different operational conditions. Some others investigations have been also reported the importance of the convection terms on the mass-transfer rate during droplet formation without providing considerable modeling.[5, 6].

In liquid-liquid extraction processes the prediction of the rate of interfacial mass transfer between two immiscible liquid phases is of paramount importance when designing extraction equipments. However, it is not yet possible to design liquid-liquid extraction equipments accurately without experimental pilot-plant information.[7, 8] General designing strategy in these equipments is based on utilization of the single droplets mass transfer information in a hydrodynamic model such as drop population balance model[9] or a statistical model as in a Monte Carlo simulation.[10] Therefore, single droplet studies are an essential basic research in these problems. Nevertheless, current single droplet models have noticeable shortcomings for predicting mass transfer rate in wide ranges of formation time and operational conditions.[4, 5, 6, 11] Thus, more investigations on single drops mass transfer are required.

When a liquid is injected into another liquid at low velocities, drops are formed which detach and break off from the nozzle. At a velocity above a certain critical value, the *jetting velocity*, a jet forms, rises to a certain length and then breaks up into drops. There are three distinct periods or stages in the lifetime of drops: formation, free-fall, and coalescence. In attempts to study and measure mass transfer during drop fall/rising period alone, mass transfer occurring during formation and coalescence has been considered as a “end-effects”. End-effects have usually been estimated by varying the column height and extrapolating the total measured mass transfer to zero height. By means of the extrapolation method and by employing experimental techniques, which eliminated the coalescence end-effect, a vast range and noticeable portion of total mass transfer was found for formation stage. For example, following results have been reported for this portion of mass transfer stage: 20 % (Coulson and Skinner, 1952)[12]; 10-50 % (Popovich, 1964)[13]; 3-39 % (Skelland and Minhas, 1971).[14] Recent experimental research also shows a noticeable mass transfer around 40 % during drop formation (Lee, 1998, 2003).[15] These works and others such as Clift et al. (1978)[16] Heideger and Wright[6] (1986), demonstrate the importance of the formation stages in liquid-liquid extraction equipments.

However, as previously noted current models can not predict mass transfer rate in wide ranges of formation time and operational conditions. For example, a significant improvement in prediction of mass transfer during drop formation obtained by Walia and Vir model[2,3] (1976a, b) using accounting the effects of the boundary curvature, convective flow around a forming drop, and the time-dependent concentration change in the continuous phase near the drop. Nevertheless, their model has failed to accurately predict the Liang and Slater experimental data[4] (1990) while circulation/diffusion model developed by Liang and Slater[4] (1990) showed good agreement with experimental data in that cases. On the other hand their diffusion/circulation model in that work showed some shortcomings when nozzle Reynolds number $(\rho_d d_N V_N A \ / \ \mu_d) < 10$. Also both above mentioned models couldn’t provide a good prediction on the Zimmermann (1980) experimental data.[17]

In this research an attempt was made to introduce a new approach for evaluating mass transfer during drop formation via defining a parameter related to the extent of the convective mixing within the growing drop. For this purpose, it was assumed that the entrance of the dispersed flow into the growing drop from the nozzle is analogous to the entrance of the flow from a smaller channel to a larger one (the expanding drops). This transfer mechanism presented in this article has been dubbed the “flow expansion”. Comparison of the results of the flow expansion model with different experimental data and other models[2-6, 17] demonstrated the significant capabilities of this new approach for estimating mass transfer during droplet formation in wide ranges of operational conditions.

Literature Review

Drop formation in liquid-liquid systems has been studied both experimentally and theoretically for the regimes before and after jetting. These studies have generally investigated the hydrodynamics aspects, and a few studies have considered the mass transfer aspects.

As the flow expansion model for evaluating the mass transfer during drop formation involves some hydrodynamic aspects, in this section some of these works in both hydrodynamics and mass transfer aspects have been reviewed.

Hydrodynamics of Drop Formation

Efforts for understanding and modeling of hydrodynamics of droplet formation on the nozzle have a long story in the following six levels:

Basic explanation of the static drop formation

This is by Tate[18] and Bashforth and Adams[19] (taken from Chazal and Ryan[20]).

Basic studies for surface science applications

This is by Lohnstein[21] (taken from Miller et al.[22]). A growing droplet and its detachment on a nozzle have been studied in surface science applications to measure surface tension and adsorption process across interfaces. Among the numerous methods for measurement of the surface tension of a liquid or the interfacial tension between two liquids, the drop volume method has gained a reputation as a standard technique.[22] The theoretical basis of the drop volume method was founded at the beginning of this century by Theodor Lohnstein.[21] He developed a basic understanding of the drop volume method and a criticism of the so-called law of Tate. The law of Tate is the basis of the calculations of surface tension from stalagmometer experiments. Lohnstein made detailed calculations of the volume of detaching and residual drops as a function of the capillary radius and the capillary constant and found systematic deviations from the law of Tate.

Early acceptable correlation for static conditions

This is by Harkins and Humphrey,[23] (taken from Chazal and Ryan,[20]) and Harkins and Brown[24] (taken from Null and Johnson,[25]). They derived an expression for calculating the droplet volume at negligibly small flow rates by equating the buoyancy and interfacial tension forces and correction factor for the fraction of liquid that remains attached to the nozzle after drop break off.

Development of models for dynamic conditions

This is by Hayworth and Treybal[26] and Null and Johnson.[25] They attempted to predict drop size as a function of variables like interfacial tension, viscosity of continuous phase, nozzle diameter and flow rate of the dispersed phase. Hayworth and Treybal[26] were the first authors to give a semi-empirical model based on a force balance made by expressing the various contributing forces acting on the drop volume under dynamic conditions. They extend the Harkins and Brown analysis by incorporating into the force balance the interfacial and drag forces that arise for finite injection velocities. Their experiments were conducted using different nozzle sizes and various liquid/liquid pairs. Their results indicated that drop size was increased by increased interfacial tension, reduced density difference between the two phases, increased viscosity of the continuous phase, and increased nozzle diameter. It was also found that drop size was independent of the fluid being dispersed and showed negligible sensitivity to the dispersed phase viscosity.

Null and Johnson[25] have presented experimental relations, based on the observed geometry of the drops. Their results are given in dimensionless groups, such as Weber, Froude, and Laplace numbers.

Development of two-stage droplet formation models

This is by Rao et al.,[27] Scheele and Meister,[28] Heertjes et al.,[29,30] Chazal and Ryan,[20] Miller and Fainerman,[22] and Barhate et al.[31] It seems, among these two-stage droplet formation models, Rao et al.[27] were the first who presented this modeling strategy. They reported that Hayworth and Treybal's[26] correlation is probably not completely justified since the exact instance at which the forces act is not known nor is their quantitative contribution to the total volume. Thus, they proposed the two-stage approach for incorporating more hydrodynamic effects on the droplet formation process. During the first stage (static stage), the drop is assumed to expand until the buoyant force balances the interfacial tension force. The drop volume at the end of the static stage is given by the equation of Harkins and Brown.[24] During the second stage, when the drop is detaching from the nozzle, the drop continues to grow.

Scheele and Meister's[28] research is a more sophisticated model for drop formation at low velocities in liquid-liquid systems. They reported that although Rao et al.'s[27] analysis significantly reduces the error for many systems, it has some weaknesses, the most evident of which is its inability to predict a drop volume smaller than that given by the Harkins and Brown analysis. In a series of publications, Meister and Scheele[32-34] worked to develop an understanding of the jet and drop formation based on experiments performed with 15 different liquid-liquid systems. They described the general behavior of the jets as follows: For low flow rates drops form, grow, neck, and break off from the nozzle at regular intervals; above a certain critical velocity, a jet is formed that rises to a certain length from the nozzle, at the point where it breaks up into drops; at still higher nozzle velocities, the jet breaks up into small drops. Much of the earlier literature on liquid-liquid drop and jet formation have been reviewed by Meister and Scheele.[34]

Heertjes et al.[29,30] reported that the drop growth during release in Scheele and Meister's[28] analysis was handled neglecting a few important phenomena, that is, kinetic and interfacial tension forces. Also, utilization of the Harkins and Brown factor is open to objection because this factor was determined for static conditions, i.e., at infinitely slow drop formation. They developed a more detailed two-stage model for drops formed at non-wetted capillaries in liquid-liquid systems. Their model incorporates essential variables in the second stage, which are the forces acting upon a drop, the way the dispersed phase enters the drop, the necking of the drop as a function of time, and finally the velocity of rise of the neck. They also obtained an experimental relation for the leading-edge velocity. They compared their model with their experimental data obtained from isobutanol drops in water saturated with an isobutanol system and also from ethylacetate drops in a water-glycerol mixture, 80%/20% system. They observed good agreement between predicted and experimental data. They also compared their model with other published experimental data. Their correlations predicted the drop's volume within an accuracy of ca. 15% for all flow rates below the jetting velocity.(Heertjes et al.[30]) Although their more detailed analysis incorporates with a dynamic Harkins/Brown factor and can obtain some improvement in some operational conditions, it involves many calculation parts and constants, and seems more complex than Scheele and Meister's analysis.[28]

Development of special correlations based on the two-stage droplet formation concept has also been considered in surface science applications. In order to estimate the true surface tension values, the drop volumes have to be corrected taking into account the hydrodynamic effects during droplet formation.[22] Several attempts have been made to perform this task, and the results have been published in the literature. Miller and Fainerman[22] recently have presented a detailed investigation on the drop volume technique based on previous works of Miller et al. and others' published works.[22] In their research, after a brief historical introduction on the development of this method, the principle of a droplet volume method and experimental set-up have been presented. Three different measurement modes, including: dynamic, quasi-static, and static, have been explained based on the hydrodynamic influences during growing of the droplet in their work. They developed a simple correction model based on a drop detachment time concept to obtain the corrected surface tension. Their data, corrected with respect to drop growth and hydrodynamic effects, provided excellent agreement between their method and others'. Miller and Fainerman[22] have also shown that the fast video technique could be of help to give an insight into the elementary processes of drop formation and detachment. It was even possible to visualize the surface waves postulated to be responsible for the drop volume bifurcations in the process of fast drop formation. Their experimental data showed good agreement with theoretical results until the drop starts to detach. However, they indicated that after the start of the detachment process a remarkable deviation between the data points and the theoretical curve can be observed.

Barhate et al.[31] reported that models proposed in the literature for prediction of the drop volume of aqueous/organic liquid-liquid systems are successful only under restricted conditions, because of the complexity of the drop formation process. Further, drop volume estimated using these models deviated considerably from the values in the case of aqueous two-phase systems. They developed a two-stage model based on Rao et al.'s[27] analysis to incorporate the Hadamard-Rybzocynski equation for the drag force with internal circulation. Their results showed some improvement in prediction of volume of drop formation at high dispersed flow rates where the polyethylene glycol rich phase is dispersed into the salt rich phase. However, they reported that the results obtained from Rao et. al.[27] in some cases where a salt rich phase is dispersed in the polyethylene glycol rich phase showed a better agreement with the experimental data. They noted that at still higher flow rates, neither their proposed model nor previously reported models could predict the drop volume satisfactorily.

Computational fluid dynamic (CFD) simulation

An analysis of the droplet formation process should involve the solution of the full Navier-Stokes equation along with the proper boundary conditions. However, the mathematical complexities of the equations, considering the existence of a free boundary two-phase flow, preclude this approach to the problem. As an alternative, an overall momentum balance on the forming drop is used, which is reviewed in the previous four sections. Recently, numerical simulation methods solution of the full Navier-Stokes equations has become available and is soon going to become practical for problems having moving interface between two different phases, based on previous basic research such as Nichols et al.[35] and Unverdi and Tryggvason,[36] with more development of these methods and other various attempts. Notable studies by Richards et al.[37,38] were the first that applied direct numerical simulation with the volume of fluid (VOF) method for drop formation in liquid-liquid systems before and after jetting conditions. Comparing their simulation results with experiments of Meister and Scheele[33,34] demonstrated the applicability of direct numerical simulations for these problems.

A similar numerical simulation method (SOLA-VOF)[35] along with experimental research was done by Ohta et al.[39] for the analysis of the single drop formation process under pressure pulse condition for a toluene dispersed phase and water as continuous phase liquid-liquid systems. Their numerical results agreed approximately with the observed phenomenon.

Zhang[40] provides another numerical (VOF/CSF) method along with experimental research for studying the dynamics of drop formation in viscous flows in a 2-ethyl-1-hexanol (2EH)/distilled-water liquid-liquid system. This work is one of the best recent numerical/experimental studies on the drop formation problem in liquid-liquid systems at dripping conditions. They solved the transient Navier-Stokes equation for the axisymmetric free-boundary problem of a Newtonian liquid that is dripping vertically and breaking as drops into another immiscible Newtonian fluid. Their numerical simulation results showed an excellent agreement with the experimental data.

Zhang[40] reported that the special feature of VOF along with the continuum surface force (CSF) scheme for incorporating the interfacial tension is a powerful numerical algorithm that allows free surfaces to cross the computational mesh smoothly, ensuring that the calculations pass the point of necking followed by natural breakup of drops without interruption, which is a major incentive for using the VOF/CSF. Homma et al.[41] reported that the VOF method deals robustly with the jet interface, especially for the pinching off or breakup into drops. The pinching off behavior may, however, depend strongly upon both the resolution of grids and the discretization scheme for the advection of the volume of fraction function (F) that determined the interface position, because F-value is assigned to each cell and the equation is hyperbolic. Although the interfacial tension effects are very important in the liquid-liquid jet issuing problem, the curvature and the normal direction, which are essential to determine the interfacial tension, may be inaccurate because the F-value distribution does not give the interface shape explicitly.

Homma et al.[41-43] also simulated formation of a jet in a liquid-liquid system and its breakup into drops using the front tracking/finite difference method. Their simulation results indicated a good agreement with experimental data. They examined how the jet and drop shape dynamics changes with the Reynolds, Weber, and Froude numbers and viscosity ratios. They reported that numerical simulation with the front-tracking method is applicable to the jet issuing problem with a wide range of conditions as well as industrial operations.[41]

Mass Transfer During Formation

Although there are vast experimental, theoretical, and numerical studies on the dynamics of droplet formation in liquid-liquid systems, the evaluation of the mass transfer during droplet formation is rather complex and there is little research on it. The instabilities associated with mass transfer during drop formation and detachments are well documented experimentally, though without significant theoretical explanation.[1] Furthermore, measurement of mass transfer during drop formation involves many operational difficulties because it generally occurs in a short time (such as 0.25-5 s) and length (such as 2-10 mm) scales at no accessible environment (top of submerged nozzle) and, as a result, includes some uncertainty.

Consequently, modeling and simulation of this phenomenon is rather complex due to the presence of a variable, flexible, permeable interfacial free boundary. In this section, a summary of history and the trend of understanding and modeling of this challenging phenomenon are reviewed at the five following levels.

Early experimental studies

Efforts for understanding, evaluation, and modeling of this phenomenon started many years ago by authors such as Whitman et al.,[44] who investigated absorption of CO_2 by water drops in a small column of constant height (taken from Groothius and Kramers[45]). They indicated that there were three distinct periods or stages in the life-time of drops or bubbles, i.e.: formation stage, free fall stage, and coalescence stage. They varied the time of formation and by extrapolation to zero formation time, found the amount of gas absorbed during the free fall of the drop. Assuming this to be constant, they calculated the absorption during formation by subtracting this constant value from the total amount of mass transfer. More than 20 years later, the concept of three stages was more clearly presented and analyzed experimentally by several investigators, such as Sherwood et al.,[46] Licht and Conway,[47] Dixon and Russell,[48] Licht and Pansing,[49] and Dixon and Swallow,[50] (taken from Popovich et al,[13]).

The first experimental work for this phenomenon in a liquid-liquid system involved trains of drops reported by Coulson and Skinner.[12] They used a different method for measuring mass transfer during drop formation. They formed drops on the tip of a nozzle, suspending them in the continuous phase, and let them disappear back into the same nozzle immediately after formation. They reported that the mass transfer fraction end effects (formation and withdrawal) have an amount of about 40% of the total transfer for the 33 cm column and the portion of the formation stage is nearly half of this amount. They reported that extraction efficiency increased slowly with drop formation time (t_f), but for the value of $t_f > 5$, the increase was very small, and therefore the rate of extraction (mass transfer coefficient) should decrease very rapidly. Their results for transfer coefficient in the benzene-benzoic acid-water showed $K_w = cte \times t_f^{-0.7}$ in comparison with the results from the Higbie penetration theory. which indicates $k = 2\sqrt{D/\pi} \times t^{-0.5}$. This comparison demonstrated the effects of the convection during the growth of a free boundary droplet on the mass transfer rate in comparison with the pure diffusion interfacial boundary. It can be seen in the next section that the early diffusion based models generally had this drawback.

Early general diffusion based models

Nearly all of the early analytical models for prediction of mass transfer during droplet formation were based on the unsteady-state diffusion theory utilizing Higbie's penetration theory, with different assumptions about the hydrodynamics of the process. Most proposed models invoked the assumption of either the surface stretch (Ilkovic,[51] Michels,[52] or Angelo et al.,[53]) or the fresh elements (Groothius and Kramers,[45] or Beek and Kramers,[54]) or engaged both mechanisms (Heertjes and DeNie,[55]). The difference among these models concerns the way the surface of the growing drop is refreshed. The first mechanism is based upon stretching of the surface. In this model, all elements remain at the surface and stretch as the drop grows. The second mechanism describes the growth of a drop by adding fresh elements to the surface.

These approaches and others have been summarized by Popovich et al.[13] They considered a general time-dependent surface area $A = \pi d_f^2 t_f^{-2/3} t^{2/3}$ when the drops are taken to be a sphere growing at a uniform rate. Also, they noted that the prediction of the several models for cumulative mass transfer is numerically different but all suggest the same dependence on physical parameters and the same exponent in the time dependence:

$$N_A = (cte)(C_S - C_0)(D\pi)^{1/2} d_f^2 t_f^{-2/3} t^{7/6} \tag{1}$$

where c_s = saturation concentration, c_o = initial concentration, d_f = final equivalent spherical diameter, t_f = total drop formation time, and D = mass transfer diffusion coefficient. Predicted values for the constant in Eq. 1 are 3.1 for the surface stretch assumption and 1.52 for the fresh surface assumption using an innovative formation-withdrawal technique to evaluate drop formation mass transfer.

Popovich et al.[13] tested the various models represented by Eq. 1 and found that the surface stretch approach is one of the best fits for their results. However, Heertjes and DeNie[55] employed a short column to minimize mass transfer following formation and obtained results more consistent with the fresh surface calculation. Rapid drop formation must necessarily result in internal drop circulation, which will then strongly influence the observed mass transfer.[6]

Growing drop and surface science applications

Interfacial mass transfer problems during droplet growing have also been noticed in adsorption kinetics studies of solutions containing surface-active agents. The growing drop (GD) method, consisting in the measurement of the dynamic interfacial tension while the surface area is continuously increasing, is an offered procedure for investigating the adsorption dynamics.[56]

The first model to describe the adsorption at the surface of a growing drop was derived by Ilkovic[51] in 1938. The boundary conditions were chosen such that the model corresponded to a mercury drop in a polarography experiment. These conditions, however, are not suitable for describing the adsorption of surfactants at a liquid drop surface.[22] The first physically founded model for interfaces with constant interfacial area was derived by Ward and Tordai.[57] It was based on the assumption that the time dependence of interfacial tension, which can be directly correlated to the interfacial concentration Γ of the adsorbing molecules, is caused by the transport of molecules from the bulk to the interface.[22] In the absence of any convection or external disturbances, this transport is controlled by diffusion. In the late 1940s, Addison and coworkers[58] made the attempt to take into consideration the area change caused by drop growth.[22] This procedure was a semi-empirical process and consisted of a step-wise calculation of $\Gamma(t)$ from the results of Ward and Tordai in a certain time interval, and a stepwise correction of the surface coverage inversely proportional to the area increase in the same time interval. This way of area change consideration, however, does not take into account any flow in the bulk phase and, hence, is only an estimate.[22]

In dynamic conditions in which the drops are continuously growing until detachment, this condition is not fulfilled and the change of the drop surface area as well as the flow inside the drop has to be taken into consideration. A first attempt to present a complete description of the adsorption process at a growing drop surface was made by Pierson and Whittaker,[59] who presented the initial and boundary condition problem based on diffusion as well as a mixed diffusion-kinetic-controlled adsorption mechanism. The numerical evaluation of the problem, however, was not satisfactory and was in contrast to experimental findings.[22]

In analogy to Ward and Tordai's[57] analysis, a rather complex integral equation was proposed by Miller.[60] A numerical analysis of this integral equation showed that the rate of adsorption at the surface of a growing drop with a linear volume increase, as is the case in drop volume experiments, is about 1/3 of that at a surface with constant area.[60] Miller and Fainerman[22] reported that the approximation for the effective age of 1/3 of the drop formation time is sufficiently accurate to interpret dynamic interfacial tensions, based on others' experiences. This means also that the same approximation (1/3) can be acceptable for other kinetic models.

An advanced theoretical analysis of the adsorption process at growing drop surfaces has been performed by MacLeod and Radke.[61] In contrast to the previous theory, they did not assume a point source at the beginning of the process but instead a finite drop size. On the basis of an arbitrary dependence of droplet radius on time "$R(t)$," a theory of diffusion- as well as kinetically-controlled adsorption was then derived. In addition to the diffusion equation, a modified boundary condition also has been proposed in their work. Their complex equation takes into consideration the function of $R(t)$ and, hence, any $A(t)$ resulting from experiments with growing drops.[22]

A good review on the state-of-the-art of the theoretical modeling and experimental investigation of the adsorption dynamics of surfactants at liquid-liquid interfaces has been reported by Ravera et al.[56] After a brief introduction to the problem of adsorption dynamics, the principal models utilized to describe the process at liquid-liquid interfaces under different assumptions, underlining the influence of the surfactant partitioning with respect to the relative volumes of the liquid phases and of the initial partitioning conditions, have been presented in their work.

Development of convection incorporated models

The necessity to develop improved mass transfer drop formation models that integrate convection and internal circulation with the molecular diffusion has been demonstrated by several investigators, including: Heertjes et al.,[62] Rajan and Heideger,[5] Skelland and Minhas,[14] Humphrey et al.,[63] Walia and Vir,[3,4] Zimmermann et al.,[17] Heideger and Wright,[6] Slater et al.,[11] and Liang and Slater.[2]

In a photographic study of the drop formation, Rajan and Heideger[5] reported a significant effect of internal convection on the measured mass transfer coefficient though the mass transfer resistance was mainly in the continuous phase. Their results showed that the surface stretch model and fresh surface elements both poorly predict the total mass transferred during drop formation for rapid formation rate cases.

Heideger and Wright[6] examined the mass transfer coefficient over a wide range of formation times, such that internal drop convection was important for rapid formation rates and relatively insignificant for slow rates. They reported significant effects of internal convection on measured mass transfer coefficients for either continuous phase or dispersed phase resistance control for drops of 3-5 mm and formation time of approximately 2.5-33 seconds. They plotted time-averaged mass transfer coefficients as a function of final formation time and observed a sharp break in the obtained line at a formation time of about 7.5 seconds. They described that this was assumed to result from some transition in the circulation that occurs within the droplets during formation time. Therefore, they proposed two distinct time regimes with unique dependencies of the average mass transfer coefficients on the formation time, resulting from a change in the mechanism of mass transfer.

Walia and Vir[3,4] have been among the first investigators who presented an improved diffusion based model, taking into account the effect of boundary curvature, convective flow around a forming drop, and the time-dependent concentration change in the continuous phase near the droplet. Their model showed noticeable improvement in the prediction of mass transfer during drop formation in some cases. They also reported that in some other cases, the Ilkovic-Baird model after correcting for the effect of changing concentration would become similar to their model. Nevertheless, the Walia and Vir model has failed to describe the experimental data of Liang and Slater,[2] while the circulation/diffusion model showed good agreement in that case.

The Liang and Slater diffusion/circulation model, which was developed based on their experience from Slater et al.,[11] is one of the first drop formation mass transfer models incorporating convection effects with a different approach in comparison with the previous models in this field. They developed a practical new model for prediction of fractional solute extraction during drop formation using analogy with the Handlos and Baron model,[64] presented for free-rise drop mass transfer coefficients. Comparing the results of their model with their experimental data and others' works showed noticeable improvement for prediction of extraction efficiency when nozzle Reynolds number was $(\rho_d d_N U_N/\mu_d) < 34$, or if the nominal circulation time d_f/U_N was not much smaller than the formation time. However, their model showed some shortcomings when nozzle Reynolds number was $(\rho_d d_N V_N/\mu_d) < 10$. On the other hand, although their model showed some agreement with the experimental data of Zimmermann et al.,[17] it could not describe them with reasonable accuracy. They reported that these data have not yet been correlated in a simple meaningful manner.

Javadi and Bastani[65,66]introduced a new approach, referred to as the "flow expansion model," for evaluation of the mass transfer during drop formation. The base and development procedure of this new model, which has a different approach in comparison with all of the previous models in this field, are presented in the next section. Comparison of the results of this approach with published experimental data[2-6] in a wide range of operational conditions demonstrated noticeable improvements for estimation of the mass transfer during droplet formation for both slow and rapid formation rates.

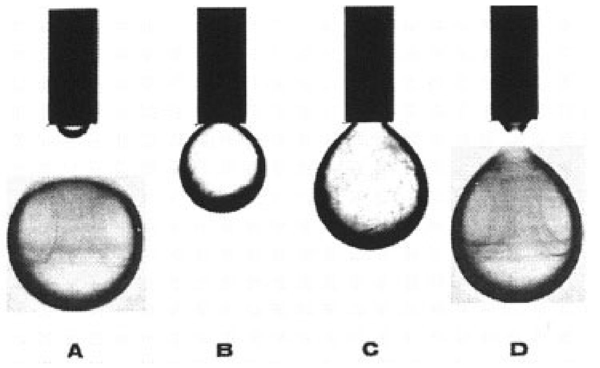

Figure 1. Typical drop formation life time.[5]

Computational fluid dynamic (CFD) simulation

A review of some published numerical works on drop formation in liquid-liquid systems (Richard et al.,[38] Ohta et al.,[39] Zhang,[40] Homma et al.,[41,42] and Taeibi-Rahni and Sharafatmand,[67]) shows that these investigations have generally evaluated hydrodynamics of this phenomenon without considering the mass transfer. Although a few CFD simulations have studied mass transfer during the rising/falling stage after formation (Piarah et al.,[68]Petera and Weatherley,[1] Homma et al.,[43] Mao et al.,[69] and Li et al.,[70]), it seems that there are very limited studies for evaluation of mass transfer during droplet formation using CFD simulation.

The Flow Expansion Model

The various mathematical models developed for prediction of the mass transfer during drop formation are generally based on a solution of the diffusion equation without any allowance for circulation within the drop. This is the main reason for the poor prediction of these models in many cases where internal convection has an important effect on mass transfer rate. Although a few investigations have developed models in which convection and circulation effects have been considered,[2-4] each had its shortcomings in different operational conditions.

In a new approach to estimate the mass transfer during drop formation, a parameter related to the extent of the convective mixing within the growing drop has been defined. For this purpose, it was assumed that the entrance of the dispersed flow into the growing drop from the nozzle (Figure 1) is analogous to that from a smaller channel to a larger one (the expanding drops). This transfer mechanism, presented in this article, has been dubbed the "flow expansion." A global time-dependent Reynolds number was defined based on the equivalent of growing drop diameter as the length scale and velocity scale obtained from the flow expansion assumption. It is shown that this time-dependent Reynolds number of a growing drop (Re_{gd}) plays an important role in the mass transfer coefficient. To proceed, however, an estimation of these length and velocity scales is required.

Evaluation of the growing drop diameter

At low nozzle velocities, Scheele and Meister[28] considered four major forces acting on the drops. For liquids injected vertically upwards and with $\rho_2 < \rho_1$, the buoyancy force due to the density difference between the liquids and the inertial force associated with the fluid coming out of the nozzle act on the upwards direction, while the interfacial tension force and the drag force associated with the continuous phase act in the downwards direction. When these forces balance, the drop begins to break away from the nozzle. Scheele and Meister[28] derived the following correlation with parabolic flow assumption in the nozzle for droplet volume ν_d:

$$V_F = F\left[\frac{\pi\sigma d_N}{g\Delta\rho} + \frac{20\mu_c Q d_N}{d_F^2 g\Delta\rho} - \frac{4\rho_d Q U_N}{3g\Delta\rho} + 4.5\left(\frac{Q^2 d_n^2 \rho_d \sigma}{(g\Delta\rho)^2}\right)^{1/3}\right] \tag{2}$$

where F_{HB} is the Harkins-Brown correction factor, which takes into account that part of the drop that remains on the nozzle after detaching, $d_N = 2R_N$ is the nozzle diameter, $Q = \bar{\nu}\pi R^2$ is the nozzle volumetric flow rate, and $\Delta\rho$ is the density difference between the two fluids. Eq. 2 shows the final diameter of the drop at the detachment time. However, we need the time-dependent size of the growing drop during formation. This size can be obtained using the following relation[6]:

$$A = \pi d_f^2 t_f^{-2/3} t^{2/3} \tag{3}$$

However, with a constant density assumption and a slight interfacial mass transfer quantity (in comparison with the growing droplet), the following simple useful relation can be obtained using the conservation of volume on the dispersed phase flow from the nozzle to the growing droplet (spherical shape assumption):

$$Q = S_N U_N = \pi R_N^2 \tag{4}$$

$$\frac{dVol_d}{dt} = \frac{d\left(\frac{4}{3}\pi r_d^3\right)}{dt} = \pi R_N^2 U_N \tag{5}$$

$$r_d = \left(\frac{3}{4} U_N R_N^2 t\right)^{1/3} \tag{6}$$

$$A_d = 10.37(U_N R_N^2 t)^{2/3} \tag{7}$$

where Q, U_N, S_N, R_N, r_d, and A_d are dispersed phase flow rate, nozzle velocity, nozzle cross-section, nozzle radius, growing drop radius, and surface area, respectively. Figure 2 shows that this simple relation is in good agreement with experimental data.

Definition of the growing droplet Reynolds number

The velocity scale is defined as:

$$u_d = \frac{S_n U_N}{S_d} = \frac{\pi R_N^2 U_N}{\pi r_d^2} = U_N\left(\frac{R_N}{r_d}\right)^2 \tag{8}$$

Consequently, the growing droplet Reynolds number can be defined as below:

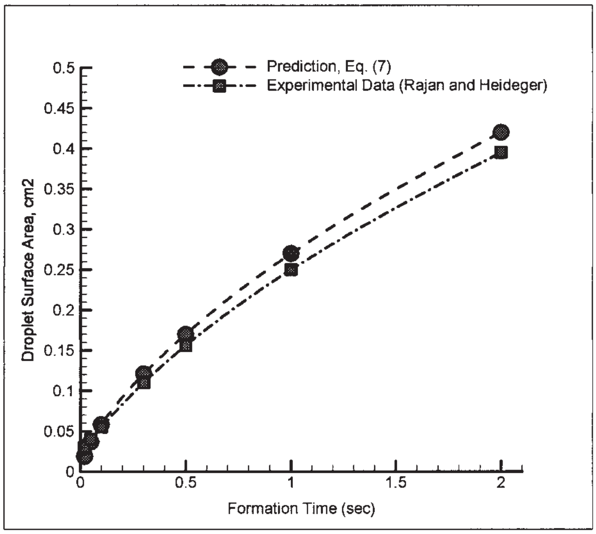

Figure 2. Estimation of growing drop surface area using Eq. 7.

$$\mathrm{Re}_d = \frac{\rho_d U_d D_d}{\mu_d} \tag{9}$$

where U_d and S_d are the velocity and cross sectional scales of the droplet, respectively, and μ_d is the dispersed phase viscosity. Substituting r_d from Eq. 6 into Eq. 9, the time-dependent growing droplet Reynolds number becomes:

$$\mathrm{Re}_d(t) = 1.1\ \mathrm{Re}_N\left(\frac{R_N}{tV_N}\right)^{1/3} \tag{10}$$

where Re_N is the Reynolds number of the nozzle. It will be shown that R_N/tV_N, which is a non-dimensional time scale, plays an important role in the mass-transfer rate. If $\tau_N = R_N/U_N$, then,

$$t^* = \frac{t}{\tau_n} \tag{11}$$

$$\mathrm{Re}_d = 1.1\ \mathrm{Re}_N(t^*)^{-1/3} \tag{12}$$

It will be shown that this time-dependent growing droplet Reynolds number has an important effect on the mass-transfer rate.

Estimation of the mass-transfer coefficients

In this section, the mass-transfer coefficient will be estimated using the growing droplet Reynolds number. To achieve this objective, typical semi-empirical mass transfer correlation between Sherwood ($_{FL/CD}$), Schmidt (υ/D), and Re numbers that are available for the constant droplet shape at rising/falling stages, is modified for the growing droplet in formation stage. A typical relation in this field can be written as[71,72]:

$$Sh = f(\mathrm{Re}, Sc) = C_1 \mathrm{Re}^{n1} Sc^{n2} + C_2 \tag{13}$$

where υ is the kinematics viscosity and D is the diffusion mass transfer. Values of $n_2 = 1/3$ and $n_1 = 1/3$ for the stokes regime, 1/2 for the boundary layer theory, and 2/3 for the refresh surface assumption or turbulence condition, were proposed.[73]

These correlations can be used for prediction of the mass transfer in continuous or dispersed phases, taking suitable values for the constants. However, they are not applicable during droplet formation, because of variation of the mass transfer mechanism during formation. Our "flow expansion" model was aimed at solving this problem via a time-dependent growing droplet Reynolds number. First, we chose $n_1 = 1$, because the flow regime during droplet formation is close to the turbulent flow due to interaction of two immiscible continuous and dispersed phases at the end of the nozzle (especially at the first stages of the growth for high dispersed flow rates and small size nozzles). However, better values for the constants can be derived from experimental data. In a liquid-liquid system, the following typical relation can be written for estimating the mass-transfer rate (with assumption of constant components and their properties):

$$Sh \propto Sc^{1/3}\mathrm{Re}^n \tag{14}$$

$$K \propto \frac{CDSc^{1/3}\mathrm{Re}^n}{l} \tag{15}$$

where l = length scale is the radius of the droplet. Therefore, the mass-transfer coefficient will be:

$$K = C_1 CDSc^{1/3}\mathrm{Re}_N^n R_N^{-1}(t^*)^{-n-1/3} \tag{16}$$

where C = concentration and C_1 is a constant for calibration of the model. Eq. 16 shows that the mass-transfer coefficient "K" is a declining function of the non-dimensional time "t^*."

As noted previously, the constant n has a variable value 0.33-1 related to the extent of the internal convection within the droplet. Therefore, its value should be selected based on a relevant factor related to the turbulence intensity within the droplet. For this object, the following typical simple relation is proposed:

$$n = n_0 + \Delta n \tag{17}$$

$$\Delta n = \log \mathrm{Re}_N^m - 1 \quad \text{for} \quad \mathrm{Re}_N > 10. \tag{18}$$

where a typical value $n_o = 0.5$, and $m \approx 1/2$ seems suitable, for enforcing $0.5 < n < 1$. Although this typical relation could approximately support our model in a wide range of operational conditions, this isn't an absolute range; and in some cases, other values out of this range such as $0.33 < n < 1.2$ may produce better results. Dependency of the accuracy of the droplet formation mass transfer models to the nozzle Reynolds number has also been reported by Liang and Slater.[2]

Results and Discussion

The evaluation of the proposed model was examined by comparison of the predicted results with published experimental and analytical results in a wide range of operational condi-

Table 1. Physical Properties* of Ethyl Acetoacetate[5]

Acetoacetate (24°C)	
Density	1.022 g/cc
Viscosity	0.0138
Diffusivity	g/(cm · s)
Interfacial tension	1.26×10^{-5} cm^2/s
Solubility in water	3.5 dynes/cm
	14.4 g/100 cc

*As listed in Handbook Chem. Phys. And Int. Critical Table.

tions. The results of the model for the prediction of instantaneous mass-transfer coefficients were compared with experimental work of Rajan and Heideger.[5] There are no previous meaningful correlations for prediction of these experimental data.

The capability of the model for prediction of cumulative total mass transfer was also evaluated via the following experimental and analytical data: Rajan and Heideger,[5] Walia and Vir model,[3,4] Zimmermann et al.,[17] Heideger and Wright,[6] and Liang and Slater.[2]

It should be noted that the experimental analysis of mass transfer during droplet formation has its own uncertainties due to the complexity of this phenomenon. On the other hand, development of analytical and semi-empirical models for prediction of mass transfer during droplet formation has its own complexity. In fact, there isn't a good analytical or semi-empirical model that can predict this phenomenon in a wide range of operational conditions (formation time, nozzle velocity and diameter, droplet final diameter, properties of dispersed and continuous phases, and so on). Nevertheless, comparing the results of the flow expansion model with various experimental data and models would demonstrate the capability of this new approach for the prediction of mass transfer during droplet formation.

Prediction of the instantaneous mass-transfer coefficients

Two-component, two-phase system experimental data reported by Rajan and Heideger[5] were considered for the evaluation of our results. An organic liquid with water solubility in the range of 10 to 25 wt % was chosen for the dispersed phase, and water was chosen for the continuous phase. The organic phase was presaturated with water in order that only one-directional transfer would occur, with the resistance to mass transfer entirely in the aqueous phase. Ethyl acetoacetate, with physical properties listed in Table 1, was selected as the dispersed phase material. The ranges of operating parameters are listed in Table 2.

The capability of the model with respect to the variation of the dispersed phase flow rate (nozzle velocity) is shown in Figure 3. A good agreement between experimental data and flow expansion model predictions can be observed for three dispersed flow rates (Q = 0.396, 795, and 0.1.372 cc/min).

Table 2. Operation Parameters[5]

Gauge No.	O.D., in.	I.D., in.
16	0.065	0.047
18	0.049	0.033
20	0.035	0.023

Dispersed Phase Feed Rate: 0.396 to 1.584 cc/min.
Continuous Phase Flow Rate: 2.7 to 11.1 cc/min.
Continuous Phase Reynolds Number: 15.7 to 64.7.

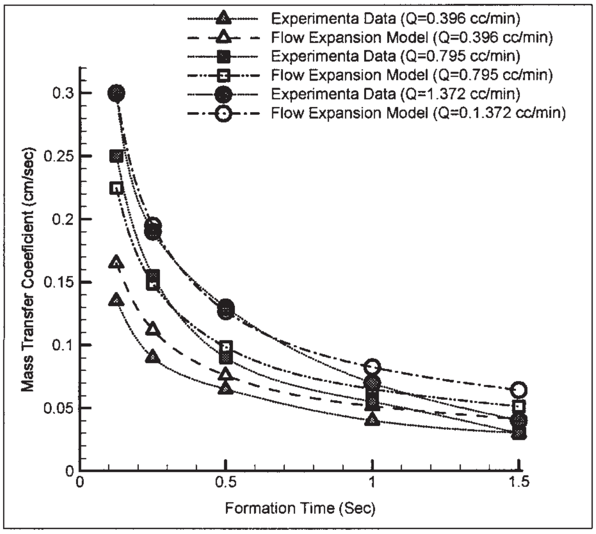

Figure 3. The effects of dispersed phase flow rate on the instantaneous mass transfer coefficients during drop formation.

Figure 4 illustrates the comparison of the results of the model with the experimental data for prediction of the instantaneous mass transfer coefficients in which the Reynolds number of the continuous phase is 15.7 and the dispersed phase feed rate is Q = 0.7953 cc/min. This Figure shows a relatively good agreement with experimental data for 16, 18, and 20 (gauge) nozzle sizes. This Figure demonstrates the capability of the "flow expansion model" to predict the instantaneous mass transfer coefficient during droplet formation for both large and small diameter nozzles that have different levels of mass transfer rate due to different internal convective mixing

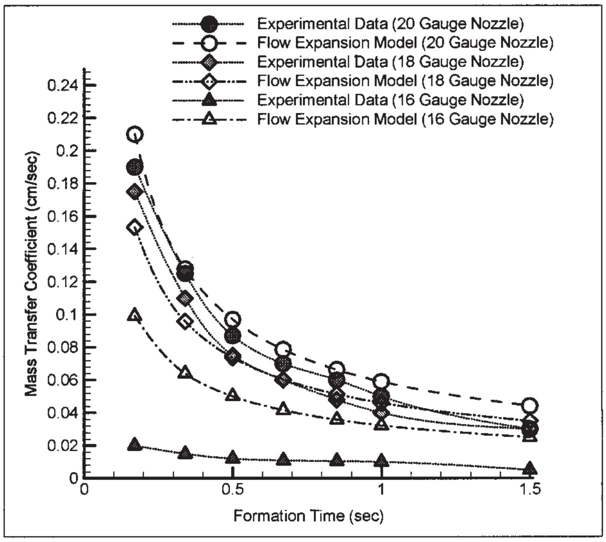

Figure 4. Prediction of the instantaneous mass transfer coefficients during drop formation—the effects of nozzle diameter.

levels within the droplet. Therefore, the model shows a relatively good sensitivity to the various levels of the internal convection inside the growing droplet, except for the beginning time of formation in the 16-gauge nozzle.

Similar discrepancy has been reported also for large diameter nozzles in others' investigations. These discrepancies will be discussed and consequently, to achieve better results in these cases, a probable modification to the flow expansion model (Javadi and Bastani[66]), employing a more accurate flow expansion mechanism during entrance of dispersed flow from the nozzle within the droplet, will be introduced. However, error and uncertainty in experimental data still remain as an obstacle in development of appropriate semi-empirical and analytical models. Furthermore, most published experimental data report the total mass transfer during formation stage, while only a few experimental data sets about instantaneous mass transfer coefficients are available. Thus, more instantaneous experimental data during formation time are required for further improvement of the model.

Modified flow expansion model

In Figure 4, a relatively good agreement between experimental data and the flow expansion model can be observed. However, the results of the model for predicting mass transfer rate in large diameter nozzles (16 gauge) in comparison with the experimental data demonstrate some shortcomings. This model can be improved by applying better evaluation of the flow expansion mechanism (Javadi and Bastnai[66]). As many experimental studies indicated, rapid decreasing in mass transfer coefficients is observed in the first stages of droplet formation specifically for small diameter nozzles and relatively high dispersed-phase flow rates. Also, a significant difference in the mass transfer rate between small and large diameter nozzles can be observed in the experimental data, particularly at the first stages of formation. It seems that these two behaviors, which have caused many complexities in the prediction of mass transfer during droplet formation in a wide range of flow regimes, can be related to a transition in the flow expansion mechanism. Therefore, an initial time for expansion initiation was defined based on this physical concept.

In this improved flow expansion model, an initial time for expansion initiation (T_e) higher than $J \times T_N$ (where T_N = *Nozzle Time Scale* $=R_N/U_N$) is required for the beginning of the droplet expansion with respect to the nozzle size (a time in which the droplet transforms to a pear-shaped form larger than nozzle diameter). A typical rough value $9 < J < 12$, can be found in reported experimental and numerical studies (Javadi and Bastani[6]). However, many parameters, especially Bond number ($\Delta\rho g R_N^2/\sigma$) should be considered in this approach. Transient concept in the flow expansion model can demonstrate that a very small nozzle time scale (T_N) and, consequently, a small T_e (e.g., less than 0.1 sec) that occurs in small size nozzles with relatively high dispersed phase flow rate, can be the main reason of the existence of these high values of mass transfer coefficients due to existence of high Reynolds number values within the droplet in the first stages of formation. On the contrary, a relatively high value of T_e (e.g., larger than 0.5 sec) enforces a noticeable restriction on initial high values of growing droplet Reynolds numbers, resulting in low observed mass transfer coefficients. In other words, it seems the maximum of practical Reynolds number value within the droplet in both cases is restricted to the nozzle Reynolds number. Thus, in the first cases, a practical high growing droplet Reynolds number ($\mathrm{Re_d}$) causes a noticeable increase in the mass transfer coefficient in the first stages of formation.

The comparison of the results of the modified model (transient flow expansion model) showed noticeable improvement in the capability of the flow expansion model in predicting mass transfer coefficients and cumulative mass transfer during droplet formation for large nozzle diameter in many cases (specifically, for large T_N cases). On the other hand, this modification shows either insignificant effects or slight improvements for other cases. In cases in which T_N has a very small value (e.g., less than 0.01 sec), this modification does not have any noticeable effect, as would be expected. It should be noted, however, that for these cases, the results of the flow expansion model without modification also show relatively sufficient accuracy.

The results of the modified model (transient flow expansion model) for predicting the instantaneous mass transfer coefficients are shown in Figure 5. In this Figure, an improvement can be observed with respect to Figure 4, especially for the initial stages of formation in 16-gauge nozzles.

The transient flow expansion model indicates that Bond number can be an important parameter on mass transfer rate during droplet formation. The importance of this dimensionless parameter on mass transfer during droplet formation was noted by Skelland and Minhas.[14] However, they included this parameter in their model using dimensional analysis. Therefore, it seems that the transient flow expansion model is the first mass transfer model that presents an acceptable mechanism about the effects of the Bond number on mass transfer rate during formation time. Indeed, the effects of any other parameter, which has noticeable effects on the droplet shape and its internal velocity, can be incorporated in the droplet formation mass transfer rate using the transient flow expansion concept.

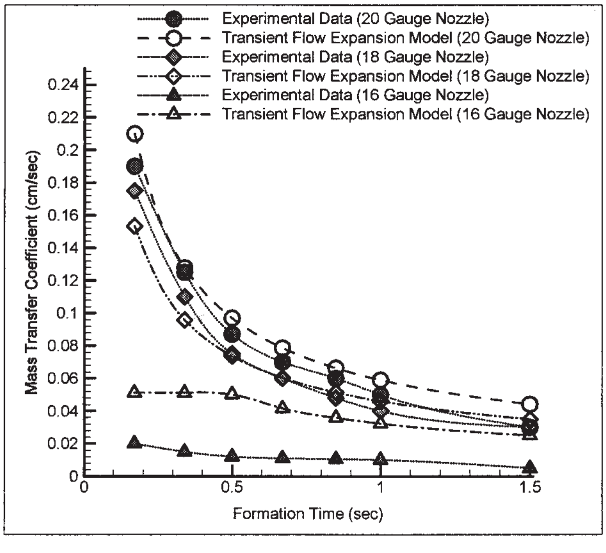

Figure 5. Prediction of the instantaneous mass transfer coefficients during drop formation, using the modified transient flow expansion model—the effects of nozzle diameter.

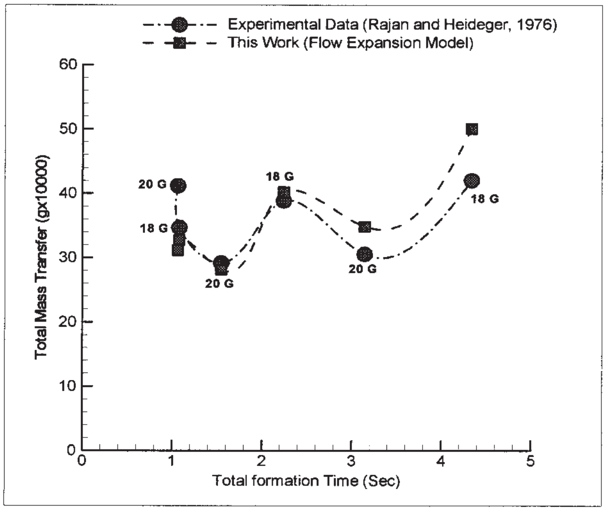

Figure 6. Prediction of total cumulative mass transfer during formation time for small and medium nozzle size (20 and 18 gauge), dispersed flow rate 0.4-1.6 cc/min and final formation time 1-4.5 s.

Prediction of the total mass transfer

In this section the capability of the model for predicting the total mass transfer during droplet formation is evaluated for a wide range of formation times. The integration of the instantaneous mass transfer was done as below by using the flow expansion model:

$$M_t = \int_0^{t_f} K(t) A(t) \Delta C dt \tag{19}$$

where M_t is the cumulative mass transfer during droplet formation. Substituting *K(t)*and *A(t)* from Eqs. 16 and 7 yields:

$$M_t = C_1 f_c f_{diff} f_{area} \frac{3}{4-n} \frac{\mathrm{Re}_n^n T_N^{(n+1)/3} t_f^{(4-n)/3}}{R_N} \tag{20}$$

where C_1 = constant of the model, $f_c = \Delta C$ (average concentration gradient factor), $f_{area} = 10.37 U_N^{2/3} R_N^{4/3}$ (droplet surface growing factor), and $f_{diff} = DSc^{1/3}$ (mass transfer diffusion factor).

The capability of the model to predict cumulative total mass transfer for a wide range of operational conditions (formation time, dispersed phase flow rate, phase components, etc.) was evaluated by comparison with Rajan and Heideger's experimental data,[5] the Walia and Vir model,[3,4] Zimmermann et al.'s experimental data,[17] Heideger and Wright's experimental data,[6] and Liang and Slater's experimental data and model.[2]

Figure 6 shows the comparison of the results of the flow expansion model with Rajan and Heideger's experimental data[5] for 18 and 20 gauge nozzles, dispersed flow rates of 0.4-1.6cc/min, and final formation times of 1-4.5 sec. A significant difference was only observed in comparison with 16-gauge nozzle experimental data, as expected. However, the results of the modified model (transient flow expansion) show a good agreement with the experimental data for 16, 18, and 20 (gauge) nozzles for dispersed flow rates of 0.4-1.6 cc/min and the final formation time of 1-6 sec in Figure 7.

Rajan and Heideger[5] reported that a square root dependence on time in relations such as $M_f = c(T_f)^n$ proposed by others, will not describe the measured mass transfer. The least square exponent was always greater than 0.5 and generally greater than 0.9. The value of n showed a considerable discrepancy, about 400% ($0.58 < n < 2.4$) in fitting with their experimental data. They indicated that this may be taken as further evidence that unsteady state diffusion alone is insufficient to describe the mass transfer occurring during drop formation. Their experimental data have not yet been correlated in a meaningful manner. Nevertheless, Figure 7 demonstrates the capability of the modified flow expansion model for tracking of the complex variations of the total mass transfer with respect to the final formation time in a wide range of nozzle diameters, dispersed phase flow rates, and final formation times.

Experimental data, along with the results of the flow expansion model in Figure 6 using Eq. 20 and the results of the modified model in Figure 7, indicate that the trend in the variations of the cumulative mass transfer with the final formation time is too complex to be predicted using simple models such as $M_f = c(T_f)^n$ or employing Eq. 1. Although many attempts have been made to predict the mass transfer during formation time using such models, the irregular shape of the curve in Figure 7 indicates that similar variations in the final formation time generally do not produce similar variations in the mass transfer rate. In order to have a practical prediction, it is important to know which parameters have caused these variations in the final formation time. In other words, sufficient information and a powerful physical mechanism are required to incorporate the role of various factors on these variations. It seems that the simple yet powerful base model of the flow expansion has noticeable capabilities for this complex task.

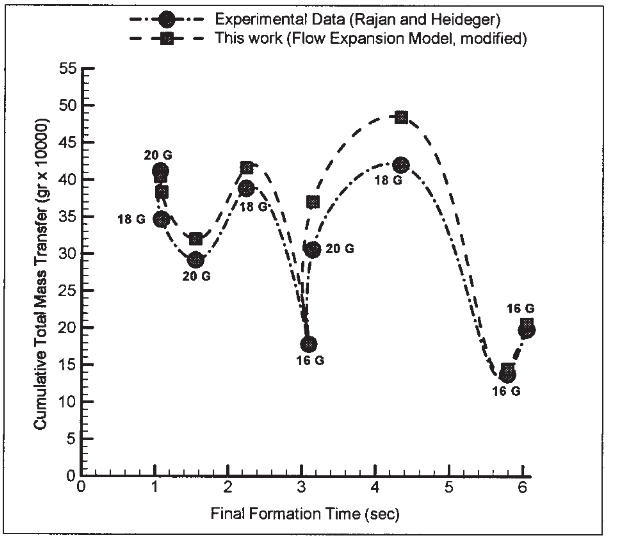

Figure 7. Prediction of the total cumulative mass transfer during formation time for small, medium, and large nozzle size (20, 18, and 16 gauge), dispersed flow rate 0.4-1.6 cc/min and final formation time 1-4.5 s.

However, more analytical, experimental, and numerical works and also further development of the expansion concept are required to achieve better results. For example, it is expected that incorporating a better hydrodynamic droplet formation model, such as the two-stage models developed by Rao et. al[27] and Scheele and Meister,[28] can improve the results of the flow expansion approach in some cases. Also, it is expected that substituting of a time dependent concentration gradient and, consequently, related variations in Eq. 19 can be useful to access better results, particularly for great interfacial mass transfer cases.

On the other hand, many other complex hydrodynamic phenomena during droplet growing and detachment on the nozzle can affect mass transfer rate. Fainerman and Miller[22] reported that the capillaries, the nozzle shape and material, and its wetting condition have important effects on the droplet formation and detachment processes. They reported that the hydrodynamics during formation has significant effects on the performance of the drop volume method at formation times of less than 10 seconds. Two main effects influencing the formation of a droplet and its detachment from the tip of a capillary, i.e., "blow-up" and "circular current," were demonstrated in their work based on literature. The first effect increases the detaching drop volume, while the second effect leads to an earlier break-off of the drop. However, the two effects act in different time windows.[22] While the circular current leads to an early drop break-off at drop times less than 1 second, the blow-up effect is effective for the drop formation time of more than 10 seconds. The importance of the nozzle shape, material, and its wetting condition on the droplet formation process have also been reported by Chen et al.[74]

At even smaller drop formation times, shorter than the range of the blow-up effect, other interesting phenomena, such as irregularities, have been reported that appear to be of chaotic character.[22] There are a few studies on chaotic phenomena during droplet formation on the nozzle. Miller and Fainerman[22] reported that to study these effects, neither of the available commercial instruments is applicable as the volume of single drops cannot be measured with a sufficiently high accuracy. For this reason, Fainerman and Miller[75] designed a special apparatus with which single drops at very small drop formation time could be studied.[22] They reported that, as a first impression, the results looked chaotic; however, there were ranges of comparatively regular drop time changes between ranges of high "scatter." Analysis of the ranges of high scatter showed that there was a kind of bifurcation—alternating larger and smaller drops. The capillary waves at the residual drop, which are not damped out completely before the next drop and which are ready to detach, are supposed to be the physical reason for the drop time or drop volume bifurcations.[22]

Thus, such investigations indicate that different complex hydrodynamic phenomena, especially in rapid drop formation cases, can exist that can produce various effects on mass transfer rate in different operational conditions, and consequently more complexities in prediction of mass transfer rate in these cases. It seems that additional improvement of the flow expansion model can be achieved with utilization of a better droplet formation hydrodynamics model (such as the two-stage models). It is expected that the flow expansion model, together with more accurate hydrodynamic models describing the evolution of the droplet size, shape, and flow field during formation, could account for the complexities of the mechanism of mass transfer during droplet formation. For example, the unexpected significant increase in the mass-transfer coefficient for the last stages of formation (for high dispersed phase flow rate cases) observed in the experimental data of Rjan and Heideger[5] could be the result of a sudden contraction-expansion in the droplet diameter during the necking process. This contraction (which can be considered as a negative expansion) can cause a significant increase in the growing droplet Reynolds number and, consequently, an enhancement in the mass transfer coefficient is expected based on the flow expansion model. Also, special two-stage droplet formation studies, such as Heertjes et al.[29,30] and Chazal and Ryan,[20] which provide some detailed information about the variations of the droplet size, velocity, geometry, and shape, could be utilized to enhance the performance of the flow expansion model in special cases.

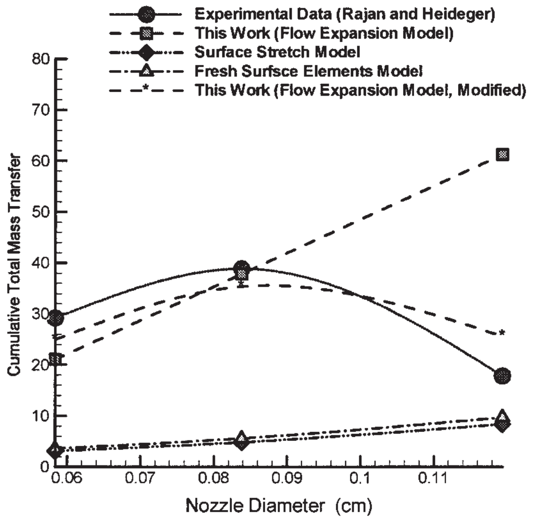

Figure 8. Evaluation of the flow expansion model relative to surface stretch and fresh surface elements models.

The potential of the model in comparison with other well-known analytical models in this field was evaluated in Figure 8, where the results of the flow expansion model for predicting the total mass transfer were compared with experimental data of Rajan et al.[5] along with the results of the surface stretch and the fresh surface elements models. The results of the flow expansion model in this Figure show a good agreement (less than 50% error) with small and medium diameter nozzles, 20 and 18 gauge, in comparison with the experimental data, while other analytical models show up to a 500-1000% discrepancy. The result of the model without modification, however, shows a significant discrepancy in comparison with the experimental data and other analytical results for large nozzles (16 gauge). The modified model (transient flow expansion model), on the other hand, shows extremely good results for this case, and demonstrates good agreement with experimental data for all three nozzle sizes. It can be observed that the results of the modified flow expansion model for both low and high internal convection intensity cases are of the same order of magnitude of the experimental data, while the results of the surface stretch model and the fresh surface elements in the cases of high and

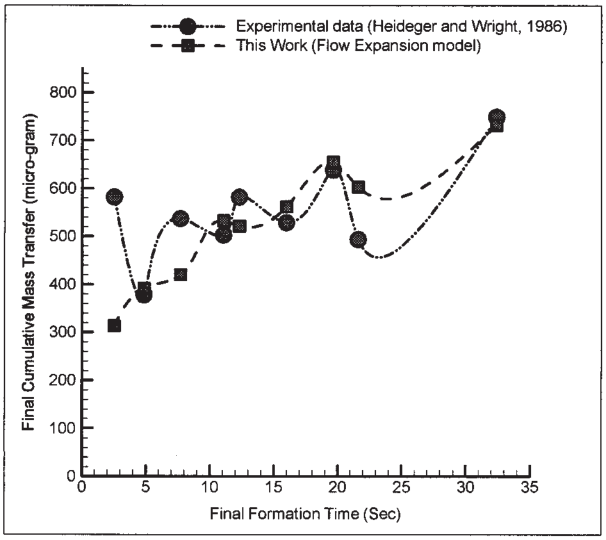

Figure 9. Prediction of total cumulative mass transfer during formation in wide ranges of final formation time.

medium internal convection regimes (18 and 20 gauge nozzles) are approximately one order of magnitude (about 500%) lower than the experimental data.

The capability of the model for predicting cumulative mass transfer in a wide range of final formation times was examined in comparison with the experimental data of Heideger and Wright. Their investigation was done over a wide range of formation times in which internal droplet convection was important for fast formation rates and relatively insignificant for slow rates. In their work, continuous phase 2-ethoxyethyl acetate was presaturated with water and the dispersed phase was water initially containing no organic component. Different formation times were obtained by various dispersed flow rates in an 18 gauge nozzle. Comparison of the results of the flow expansion model with these experimental data is demonstrated in Figure 9. Except for a few points, there is a relatively good overall agreement between model predictions and experimental data, showing the same trend for a wide range of formation times (2.5-33 s). Errors in experimental data, which are unavoidable, could be the origin of some of these discrepancies.

Prediction of the extraction efficiency

The results of the model for predicting the fraction of solute extracted during the formation time have been compared with experimental data and convection incorporated models. This comparison is illustrated in Figures 10-12, where the results of our model have been compared with Liang and Slater's[2] experimental data and their semi-empirical circulation/diffusion model, along with the analytical model of Walia and Vir[3,4] and experimental data of Zimmerman.[17]

The fraction of the solute extracted (extraction efficiency) during formation time was defined as:

$$E = \frac{C_{0in} - C_{0out}}{C_{0in} - C_0^*} \tag{21}$$

in which, C_0 shows the organic phase solute concentration, mole/liter; and since there was no solute initially in the water, $C_0^* = 0.0$ (Slater[11]). In Liang and Slater's experimental work,[2] the continuous phase was distilled water presaturated with cumene and initially containing no acetic acid, and the dispersed phase was cumene (iso-propylbenzene) containing acetic acid at about 0.25 M as solute. The temperature was about 20°C, and physical properties were given in Slater et al.'s[11] research. Figure 10 shows a good agreement between the flow expansion results and the Liang and Slater model, along with their experimental data for both flow expansion models with

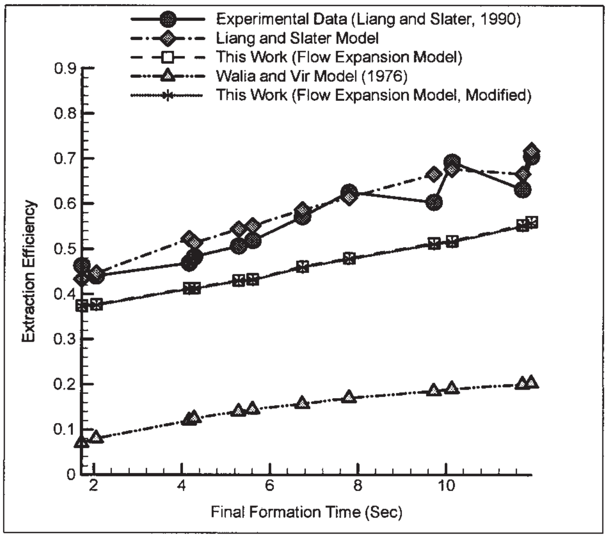

Figure 10. Prediction of extraction efficiency for small nozzle time scale cases (T_N = 0.001-0.006 sec).

Operational conditions: nozzle diameter 0.406 mm, nozzle velocity 30-195 mm/sec, and final formation time 1-13 s.

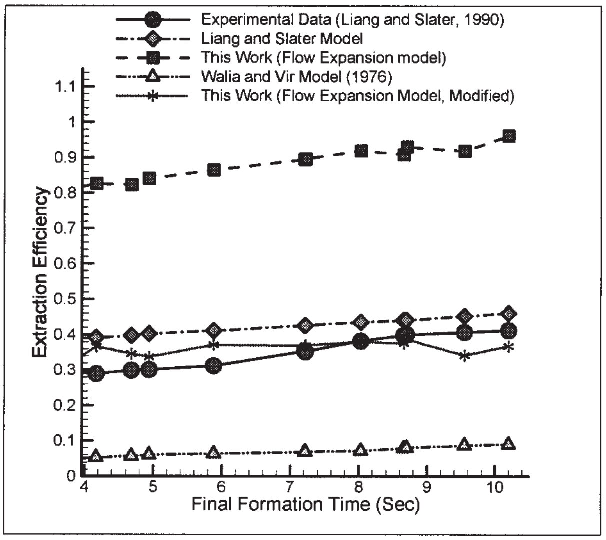

Figure 11. Prediction of extraction efficiency for large nozzle time scale cases (T_N = 0.57-3.33 s).

Operational conditions: nozzle diameter 4.0 mm, nozzle velocity 1.2-7.0 mm/s, and final formation time 4-10.5 s.

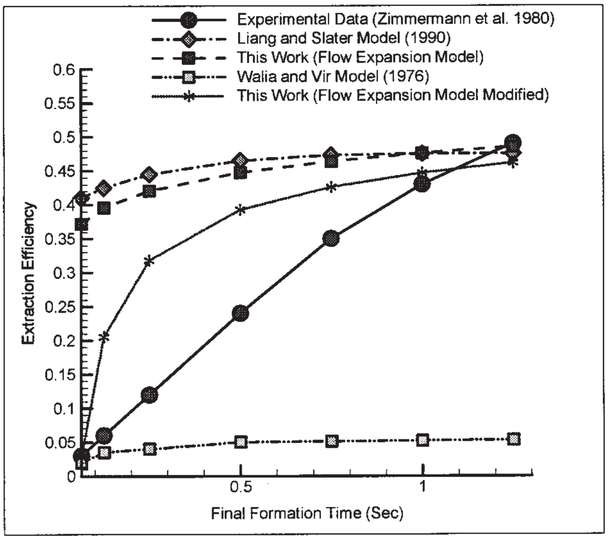

Figure 12. Prediction of the extraction efficiency in comparison with Zimmermann experimental data and other models.

and without modification. Operational conditions in this case were: a nozzle diameter of 0.406 mm, nozzle velocity of 30-195 mm/s, and final formation times of 1-13 sec. A small nozzle size and high nozzle velocity both were the main reason to have a small nozzle time scale (T_N = 0.001-0.006 s) and, consequently, a noticeable internal convection within the droplet and relatively high extraction efficiency. The results of the Walli-Vir model[3,4] in this Figure show significant discrepancy with respect to the experimental data.

Figure 11 shows another case study of Liang and Slater,[2] in which operational conditions are: a nozzle diameter 4.0 mm, nozzle velocity 1.2-7.0 mm/sec, final formation time 4-10.5 sec. Because of a relatively large nozzle diameter and low nozzle velocity and, consequently, a large nozzle time scale (T_N = 0.57-3.33 s), the flow expansion model without modification shows an over-prediction in comparison with the experimental data. On the other hand, the results of the modified flow expansion model show a good agreement in comparison with the experimental data, even a bit better than Liang and Slater's[2] model. The Walia-Vir model[3,4] in this Figure also shows a poor prediction. It seems that because of the diffusion based concept in their model, its predictive ability for mass transfer rate with significant internal convection within the droplet is rather poor.

Figure 12 shows the predicted results of the flow expansion model in comparison with experimental data of Zimmerman.[17] In this Figure, the flow expansion model shows a relatively good agreement with Liang-Slater's diffusion/circulation model. However, both models show a significant over-prediction in the first stages of formation, but converge to the experimental values in the last stages of formation. The results of the Walli-Vir model[3,4] are generally poor (such as previous cases) and only show a good agreement in the beginning of the formation for a few data points. Accordingly, it can be said that the modified flow expansion model is probably the earliest practical model that could provide a relatively good prediction on the Zimmermann[17] experimental data.

Conclusion

In this article an attempt was made to introduce a new approach to evaluate mass transfer during droplet formation on the nozzle. For this purpose, it was assumed that the entrance of the dispersed flow into the growing droplet from the nozzle is analogous to that from a smaller channel into a larger one (the expanding droplet). This transfer mechanism was called the flow expansion model.

A global time-dependent Reynolds number was defined based on the equivalent of the growing droplet diameter as the length scale, and the velocity scale was obtained from the flow expansion assumption. It was shown that this time-dependent Reynolds number of the growing droplet (Re_{gd}), which includes a non-dimensional time related to the nozzle time-scale, plays an important role in the mass-transfer process. A typical semi-empirical mass transfer correlation for the rising/falling stage, which includes the Sherwood, Schmidt, and Re numbers, was developed by employing Re_{gd} for the droplet formation stage. The results of the model for prediction of instantaneous mass-transfer coefficients and total cumulative mass transfer showed relatively good agreement in comparison with reported experimental data. However, in some cases for large nozzle diameter, and relatively low nozzle velocity, i.e., in cases with noticeable large nozzle time scale (T_N), the results of the flow expansion model indicated some shortcomings. Therefore, a modification called the transient flow expansion model was introduced. This modified flow expansion model could improve the results of the original model in those cases (large T_N) and showed a relatively good agreement with experimental data over a wide range of operational conditions, i.e.: nozzle diameter, nozzle velocity, final formation time, and various liquid-liquid systems.

The potential of the model was evaluated in comparison with available analytical and semi-empirical models. The predicted results for total mass transfer were compared with reported experimental data, along with the results of the surface stretch and the fresh surface elements models. The results of the transient flow expansion model showed a 15-50% discrepancy in comparison with the experimental data, while other reported analytical models show up to 50-500% discrepancy. In other words, the results of the modified flow expansion model for both low and high droplet internal convection regimes are of the same order of magnitude of the experimental data, while the results of the surface stretch model and the fresh surface elements in the cases of high and medium internal convection regimes are approximately one order of magnitude lower than that of the experimental data.

The comparison of the model with respect to the previous convection/circulation incorporated models demonstrates a high potential for this new approach for predicting mass transfer during droplet formation. The modified flow expansion model probably is the first practical model that could present a relatively good agreement with the experimental data of Zimmermann.[17]

It seems that additional improvement of the flow expansion model can be achieved with utilization of a better droplet formation hydrodynamics model (such as the two-stage models) for incorporating better hydrodynamic effects during the formation stage. We look forward to describing some complexities of mass transfer during droplet formation using such improvements in future works.

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Notation

C_0 = dispersed phase solute concentration
C_S = saturation concentration
D = mass transfer diffusion coefficient
d_N = nozzle inside diameter
d_f = diameter of detached droplet (equivalent spherical)
$E = C_{0in} - C_{0out}/C_{0in} - C_0^*$ = extraction efficiency during formation time
F_{HB} = Harkins-Brown correction factor
$f_c = \Delta C$ = average concentration gradient factor
$f_{area} = 10.37 U_N^{2/3} R_N^{4/3}$ = droplet surface growing factor
$f_{diff} = DSc^{1/3}$ = mass transfer diffusion factor
M_t = cumulative mass transfer during droplet formation
Q = dispersed phase flow rate
r_d = growing droplet radius
R_N = nozzle inside radius
$Re_N = \rho_d d_N U_N / \mu_d$ = nozzle Reynolds number
$Re_{gd} = \rho_d d_d U_d / \mu_d$ = Reynolds number of growing droplet
S_N = nozzle cross-section
t_f = total droplet formation time
T_e = initial time for expansion initiation
$\tau_N = R_N / U_N$ = nozzle time scale
$t^* = t/\tau_n$ = non-dimensional time scale
U_N = nozzle velocity
ρ_d = dispersed phase density
ρ_c = continuous phase density
$\Delta\rho$ = density difference between the two fluids
μ_d = dispersed phase viscosity
υ = kinematics viscosity
Γ = interfacial concentration
σ = interfacial tension

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