MASS TRANSFER DURING DROP FORMATION

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ABSTRACT

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The efficiency of a liquid-liquid extraction process is intimately connected with the methods of phase dispersion and the rates of mass transfer in and out of the dispersed phase. It is now generally recognized that extraction from a dispersed drop occurs in three stages during its lifetime :

(1) mass transfer during the formation of drops,
(2) mass transfer during the travel of the dispersed drops through the continuous medium, and
(3) mass transfer during coalescence (collapse) of the drops.

The transfer processes occurring during formation and collapse are referred to as end-effects. While a vast amount of literature has accumulated on mass transfer during the steady-state drop rise period, the information available on mass transfer connected with the end-effects is fragmentary.

Of the few attempts made to formulate extraction models for mass transfer during drop formation, the one assuming uniform spherical growth (expanding rigid sphere model) appears to have met with considerable success. A recent approach is based on the stretching and renewal of

surface elements to account for the behaviour of different parts of a growing drop. A noteworthy feature of the existing theories is that they all lead to simple final equations which are strikingly identical, and which can be put in the form

$$E = \alpha_2 \left(\frac{D t_f}{r_f^2} \right)^{1/2} \qquad \text{--- } (2.50)$$

The values of α_2 for the different models vary from about 1.5 to 6.

No theory has yet been formulated, however, which can predict the mass transfer coefficient during drop formation with any degree of accuracy. The present investigation was undertaken with three specific objectives :

(1) to develop a model for the hydrodynamics of drop growth;

(2) by using (1) to predict the mass transfer coefficient during drop formation; and

(3) to examine the proposed conceptual model using mass transfer data collected in a simple conventional apparatus.

The internal circulation created in a growing drop is induced by the jet momentum at the orifice, in contrast to the circulating patterns in a stable but moving drop which are created by the mobile spherical liquid-liquid interphase.

Thus the circulation within a growing drop (which is immiscible with the continuous phase and which is assumed to be ideal) can be attributed to the streamline motion set up inside it due to an injection velocity. These streamlines must necessarily be closed because of containment. The induced circulation is essentially independent of any viscous drag due to the velocity of growth of the drops (as against the predominant role of viscous drag in the case of Hadamard's model (29)).

At any instant the internal streamline kinematics can be likened to the lines of the magnetic field inside a spherical loss-less cavity oscillating in TE_{101} mode, the cavity being assumed to be fed through a small aperture. This permits one to solve the problem on hand in terms of its electromagnetic analogue (spherical microwave cavity in the dominant mode) by making the following identification:

	Electromagnetic	Hydrodynamic	
1)	$\vec{H}$ (magnetic field)	$\vec{V}$ (velocity)	
2)	Magnetic lines of force	Streamlines	
3)	div $\vec{H} = 0$	div $\vec{V} = 0$	(3.19)

Boundary condition :

Radial component

$\vec{H}_r = 0$	$\vec{V}_r = 0$	(3.20)
at $r = a$	at $r = a$	

The kinematic analogy arrived at in the foregoing section must not be taken too literally. In point of fact, the electromagnetic analogue (the spherical microwave cavity) admits of infinitely many modes as solution, while in the case of internal circulation in the drop in question it is only the TE_{101}-like streamline pattern which is pertinent. It is believed that the analogy is fairly exact for this dominant mode. Dynamically, the two problems are completely dissimilar in that the inertia-force relations are different. However, in both the cases the trajectory of a descriptive point can be expressed in parametric form involving space co-ordinates only, which are similar in the two cases. This in itself ensures a geometric similarity between the two analogues. The physical plausibility of the above kinematic similarity for TE_{101}-like mode is self-evident.

Based on this analogy between hydrodynamic streamlines and the magnetic force lines, theoretical equations have been developed which make it possible to estimate the streamline function of a growing drop. According to this model the centre of circulation is given by

$$r_c = 0{\cdot}609\, a \qquad --- \; (3{\cdot}41)$$

where r_c is the centre of circulation and <u>a</u> is the instantaneous radius of the growing drop. The experimental observations reported by Heertjes et al. (17) provide excellent support to this prediction and justify the proposed model.

Using the streamline function thus computed, the average time of circulation inside a drop has been calculated by programming on an IBM-7044 computer. Then, from Einstein's equation which relates the mean square deviation for a given time with effective diffusivity, it has been possible to estimate the mass transfer coefficient inside a circulating drop. The final equation obtained for the mass transfer coefficient of a growing drop is remarkably simple and is given by the single parameter equation,

$$k_i = 0{\cdot}01\ V_o$$

But since $V_o \approx V_N$

$$k_i \cong 0{\cdot}01\ V_N \qquad \text{---} \quad (4{\cdot}40)$$

where k_i is the mass transfer coefficient, V_o is the velocity at the instantaneous centre of the growing drop, and V_N is the injection velocity.

Using 4 binary systems at 25°C. experiments were conducted in a simple conventional set-up, to obtain mass transfer data in both the directions - from and to the drops. Mass transfer efficiency was determined by using an automatic potentiometric titrator. It was ensured that the solvents used were of extremely high purity as determined by several physical measurements. Comparison of the experimental mass transfer coefficients with those obtained from the mathematical model showed remarkably good agreement.

CHAPTER – 1

MASS TRANSFER FROM SINGLE DROP

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1.1 INTRODUCTION

Liquid-liquid extraction is an important industrial operation in which two immiscible liquids are contacted with each other with the object of effecting the transfer of the desired component from one phase to the other. In this operation, one phase is invariably dispersed in the form of fine drops into the other phase, thus ensuring intimate contact between the phases.

A vast volume of literature exists on liquid-liquid extraction in general, but most of the results have been presented in the form of equations based on average values of the mass transfer coefficient. In recent years, however, attempts have been made to study the mechanism of extraction in a more fundamental manner.

It can easily be visualised that the mechanism of solute transfer involves three distinct stages of extraction in the life time of a given drop. The period over which drop formation occurs constitutes the first stage of extraction. The second stage covers the period over which the drop falls or rises through the continuous phase. This stage begins at the instant the drop is detached from the tip and ends when it strikes the interphase at the opposite end of the column. The third and the final stage of extraction covers the remaining period in the life time of the drop, and consists of the process of the drop crossing the interphase at which it arrives at the end of the second stage. An authoritative review of drop phenomena as they affect liquid-liquid extraction has been presented by Kintner (34). The present work is concerned with the mechanism of extraction during drop formation (first stage of extraction).

1.2 SURVEY OF TECHNIQUES FOR DETERMINING MASS TRANSFER IN A FORMING DROP

Whitman, Long and Wang (1) made early studies of mass transfer from spray droplets, which indicated that there are three distinct periods or stages in the life time of drops and bubbles : formation, free fall, and coalescence. They investigated the absorption of carbon dioxide by forming drops of water in a small column of constant height. A series of drops was formed at a fixed formation rate at the top of the column and collected under a kerosene seal at the bottom. This was repeated for several series of drops, each series having a different formation time. A plot of formation time vs. the total amount of gas absorbed per unit volume of drop gave a straight line. Extrapolation of the line to zero formation time gave the amount of gas absorbed during the free fall of the drops. Assuming this to be constant (for a given column height), the gas absorbed during formation was calculated by substracting this constant value from the total amount absorbed. The conclusions reached were : (1) the rate of absorption during the formation of the drop is constant, (2) the amount of absorption during a fall of fixed height is constant and independent of the time of formation, and (3) the amount of absorption during this fall is always much greater than that during formation.

Sherwood, Evans and Longcor (2) studied the transfer of acetic acid from dispersed drops of methyl isobutyl ketone and benzene to a continuous aqueous phase in columns of varying heights. For a given height of column, a series of drops was formed at a constant rate at the bottom of the column and collected in a measuring burette at the top. The total acid extracted during drop formation, rise and coalescence was measured. The so-called end-effect (which presumably includes drop formation and coalescence) was determined by plotting the logarithm of the fraction unextracted (based on the concentration of the solvent phase) against column height. The resulting straight line was extrapolated to zero column height to give an end-effect of approximately 40% of the total material transferred.

The results indicated considerable agitation in the interior of each drop, and showed that a large portion of the extraction occurred during the formation of the drop.

Licht and Conway (4) confirmed the existence of three stages of extraction during the life time of a drop as postulated by Whitman et al. (1), and were among the first to attempt an experimental separation of stages 1 and 2 from stage 3. For this purpose two columns were used, the first being essentially similar to that employed by Sherwood et al. (2) in which stages 1 and 3 were estimated by extrapolation to zero column height. The second column was provided with an additional stop-cock at the bottom which was closed as soon as the last droplet had passed through it, and it was assumed that by this procedure the third extraction stage was eliminated. Then, by an extrapolation procedure similar to that for Column 1, it was believed that mass transfer during stage 1 could be estimated. From the data obtained by extracting acetic acid from aqueous drops dispersed in ethyl acetate, methyl isobutyl ketone and isopropyl ether, the following results were obtained :

	per cent extracted		
	Ethyl acetate	Methyl isobutyl ketone	Isopropyl ether
Stages 1 and 3	29	21	12
Stage 1	17	8	5

For the methyl isobutyl ketone-acetic acid system, Sherwood et al. (2) obtained a value of 40% for stages 1 and 3 as against 21% by the present investigators. This discrepancy was believed to be due to the fact that the continuous and dispersed phases were interchanged in the two studies.

It was also found that the fraction extracted during drop formation was independent of drop diameter in the range 0.383 - 0.451 cm., and of formation time greater than 1 sec. Further the overall transfer coefficient for stage 1 was found to be inversely proportional to drop size.

In another investigation similar to that of Sherwood et al. (2), West et al. (3) attempted to reproduce the results of the water-acetic acid-benzene system and, based on three other independent studies (5, 6, 7), it was concluded that approximately 14-20% of extraction occurred during drop formation as against 40% obtained by Sherwood et al. The discrepancies between the results of the two investigations were attributed to differences in the purity of the benzene used with resultant differences in some important physical properties. This was subsequently confirmed (8) when it was observed that the discrepancies were due primarily to the use of Tygon tubing in the feed system of the apparatus. When impurities are extracted from the Tygon tube, they tend to concentrate at the water-benzene interface, thus setting up interfacial barriers to transfer which account for the reduced extraction efficiency. However, the efficiency could be raised many-fold by the addition of small quantities of different alcohols (to the solvent) which tend to displace or destroy any such interfacial barriers.

In contrast to the speculation of Sherwood et al. (2) West and collaborators (3) postulated that the dispersed drops are internally stagnant.

Licht and Pansing (9) used the same columns as those employed by Licht and Conway (4) and extracted acetic acid from water with methyl isobutyl ketone as the continuous phase. Acetic acid was also extracted from perchloroethylene with water as the continuous phase. From the data obtained over a 25-fold range of drop formation time (0.4 - 10.0 sec.), it was concluded that the amount of extraction occurring during drop formation is so small that experimental results do not detect the variation with drop formation time. This observation upholds the earlier results of Licht and Conway (4) according to which the extraction efficiency during drop formation is independent of formation time when the latter exceeds 1 sec.

The work of Licht and Pansing (9) is significant in that for the first time the straight line extrapolation method of Sherwood et al. (2) to obtain the end-effect has been modified. According to their data, the linear relationship is restricted to a given range of column heights only, and fails as the height approaches zero which is the region of interest.

Garner and Skelland (10) investigated the diffusion of acetic acid from droplets of nitrobenzene falling into a continuous water phase. The steady fall (or rise) period was practically eliminated by restricting it to 4-5 mm., and it was assumed that the extraction occurred exclusively during drop formation. This analysis obviously has neglected the mass transfer during drop collapse.

These investigators varied the formation time from 2 to 50 sec. (again a 25-fold variation but with higher formation times), and observed a 2-fold improvement in mass transfer. This result apparently contradicts the earlier observation of Licht and collaborators (4, 9) who had concluded on the basis of studies with formation times not exceeding 10 sec. that any improvement in mass transfer with increasing formation time would be undetectable.

For a given outer diameter of the dispersing nozzle and time of formation, the fraction extracted during formation was found to increase with decreasing internal diameter of the nozzle. This was attributed to increased turbulence resulting from greater linear flow rate of liquid into the growing drop with nozzles of smaller internal diameter.

The overall transfer coefficient during formation was observed to fall rapidly as the formation time was increased to about 20 sec., beyond which it became nearly constant with further increase in formation time. It must be recognized that this refers to the mass transfer coefficient and not to the actual mass transfer as in previous cases. Thus, while the actual mass transfer will increase with increase in the time of drop formation, the mass transfer coefficient must decrease up to a point, after which it remains constant due to essentially molecular diffusion.

Coulson and Skinner (11) transferred propionic and benzoic acids from their solutions in water to benzene drops, and measured the transfer coefficient during drop formation by forming and immediately withdrawing the drops to the side outlet in a specially designed apparatus. The benzene entered the apparatus through a needle valve and formed a drop on the tip of a nozzle. Before the drop was detached from the nozzle tip, it was forced out of the system by the hydrostatic head of the continuous phase through a suitable side tube. This cycle was repeated holding the time of formation constant until sufficient liquid had been collected for analysis. The apparatus was operated manually and was found to be suitable for times of formation greater than 3 sec. only. For more rapid drop formation an automatic apparatus was developed. The drops were formed and removed by fluctuating the pressure at the top of the column through a small piston pump.

Extraction was found to increase over a formation and withdrawal time range of 0.515 to 14.1 sec., but for times greater than 5 sec. the increase was very small. Assuming that the transfer rate was the same during formation and subsequent withdrawal, they showed that the overall mass transfer coefficient based on the average area exposed during drop formation time is inversely proportional to formation time. However, it was found to be independent of drop size, in contrast to the observation of Licht and Conway (4) that it was inversely proportional to drop size. These investigators support the internal circulation theory mentioned earlier (2) by postulating a certain "degree of circulation" within the forming drops.

The results and conclusions presented by these workers should be analysed in the light of the following fact. In all the studies in which mass transfer during drop formation was measured by extrapolation or by any technique other than drop formation and subsequent withdrawal, the mass transfer occurs in two stages : during unsteady state drop formation, and during the unsteady state approach to steady state drop rise. In the results reported by Coulson and Skinner (11), the second effect is evidently ignored since the drop is withdrawn immediately after formation. These results therefore do not have a common basis with the other published data.

In contrast to the indirect determination of the mass transfer during drop formation in liquid-liquid systems, in the case of gas absorption it has been found possible to measure the mass transfer directly during drop formation. Work in this area, although not specifically related to liquid-liquid extraction, should be applicable to the study of the mechanism of mass transfer in forming drop.

Dixon and Russell (12) used a technique in which water drops were allowed to form at the tip of a nozzle, absorb CO_2, and then fall through a short column of the gas before being trapped under a kerosene seal (this being the most suitable liquid for CO_2). They concluded that the very high absorption rates of drops having short formation times are mainly due to the internal turbulence produced by the jet of water from the capillary which reduces the resistance to diffusion at the surface, i.e. reduces the effective film thickness. To account for the increased mass transfer during drop formation, an empirical "degree of turbulence" was introduced based on the orifice dimensions, and the drop volume. The similarity between this conclusion and the earlier conclusions (2, 10, 11) with respect to liquid-liquid extraction may be noted.

Further, as in the case of liquid-liquid extraction, reported by Coulson and Skinner (11), the absorption was found to be inversely proportional to formation time. The results of these investigators also uphold the observation of Garner and Skelland (10) that for nozzles of constant outer diameters, but varying internal diameters, the mass transfer increases with decreasing internal diameter, provided the drop formation time is held constant.

In a subsequent study Dixon and Swallow (13) presented an interesting method for eliminating mass transfer during drop collapse. Instead of a kerosene seal they investigated the use of different barriers such as : (a) a stream of inert gas moving across the collection chamber; (b) a mass of foam closing the base of the chamber; and (c) a liquid film stretching across the bottom of the chamber.

Groothuis and Kramers (14) developed an experimental method by which the amount of gas absorbed could be measured continuously at any instant during drop formation. The time of formation was varied between 1 and 40 sec. Drops were formed at the tip of a capillary in an enclosed volume containing pure SO_2. The amount of gas absorbed was determined by the measurement of pressure or volume change. It may be noted that, as in the method of Coulson and Skinner (11), the mass transfer during growth alone was measured. This fact probably explains the higher values obtained by Dixon and Russell (12) which included the mass transfer during drop release.

The experimental technique used enabled them to determine for the first time the mass transfer as a function of time (continuously) for a given formation time. Their results clearly confirm the earlier conclusion that the transfer coefficient is inversely proportional to the formation time.

An interesting feature of this work was the study of the relationship between mass transfer and jet action. A criterion was developed for establishing the influence of jet action, according to which the rate of mass transfer begins to increase due to jet action when

$$\frac{\rho \cdot V_N \cdot d_N}{\mu} > 40-50 \qquad --- (1\cdot1)$$

Rusin (15) used a photographic technique to study the mechanism of extraction of coloured solute - picric acid - from a drop of toluene forming in water. Relationships were developed to relate the darkness of a photographic image of the drop to the total amount of extracted acid and to the distribution of this acid over the surface at any instant during drop formation.

This study is interesting in that it provides for the first time a method (which is quite ingenious) for measuring the mass transfer at any instant during drop formation in liquid-liquid extraction. (Note : the method of Groothuis and Kramers (14) was for gas absorption.) The results have shown that the instantaneous mass transfer coefficient is inversely proportional to the diameter of the drop during its growth. This study also does not include the second stage of unsteady state mass transfer (i.e. during drop release) mentioned earlier.

Heertjes and Denie (26) studied a system of isobutanol drops in a continuous water phase. The drop was formed in such a way that the time of formation was independent of the frequency of the drop formation. In the experiments the final drop volume was kept constant. A short spray column with one capillary and a small surface of coalescence was used to keep mass transfer during drop rise and at the interface of coalescence as small as possible.

CHAPTER – 2

EVALUATION OF EXISTING MODELS

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In chapter 1 the various reported methods of measuring mass transfer during drop formation were discussed and certain significant results were highlighted. In the present chapter, almost all the theoretical models proposed for mass transfer during drop formation are examined and compared after reducing them to a common efficiency basis. This may be regarded as an extension of the work of Popovic et al. (22), who compared a few of the models on the basis of total mass transfer.

Apart from the empirical methods to determine the mass transfer coefficient, theoretical attempts through the solution of the unsteady state molecular diffusion equations have been made. Newman (20, 21) has solved the unsteady state molecular diffusion equation for a sphere, on the assumption that there is no internal mixing and that the sphere is stagnant with a uniform initial concentration, constant diffusivity and a parabolic concentration profile after a time. A series solution was proposed in terms of the Fourier number $\left(\frac{Dt_f}{r_f^2}\right)^{1/2}$. This solution cannot be used for mass transfer in a growing drop because at moderate drop formation times the interior of the drop cannot be assumed to be stagnant. The first acceptable theories of mass transfer during drop formation can be traced to the penetration theory proposed by Higbie (16).

2.1 COMPARISON OF MODELS

A gas diffuses through a liquid according to Fick's (or Graham's) law which, for unidirectional mass transfer, is given by

$$dN = -DA\left(\frac{dc}{dx}\right)dt \qquad \text{--- (2·1)}$$

$$\frac{\partial c}{\partial t} = D\,\frac{\partial^2 c}{\partial x^2} \qquad \text{--- (2·2)}$$

Neglecting heat and surface effects and dilatation, and assuming the diffusivity to be constant and depth infinite, the concentration at any time t is given by

$$c = c_o + \frac{c^* - c_o}{(\pi D t)^{1/2}}\int_x^{\infty} e^{-\frac{X^2}{4Dt}}\,dX \qquad \text{--- (2·3)}$$

and the integrated mass transfer at any time t by

$$N' = 2(c^* - c_o)\left(\frac{D}{\pi t}\right)^{1/2} \qquad \text{--- (2·4)}$$

This equation can be put in the standard form

$$N' = k_L \ (c^* - c_o) \qquad --- \quad (2.5)$$

where

$$k_L = 2\left(\frac{D}{\pi t}\right)^{1/2}$$

and N' is the diffusion flux.

In order to apply the above equation to the present problem the following assumptions were made :

(1) Mass transfer takes place by unsteady state diffusion into a semi-infinite medium, i.e. the velocity of diffusion is small as compared to the velocity of drop growth.

(2) The concentration at the interface (c^*) is the saturation concentration.

(3) The diffusion coefficient (based on c^*) in the direction of mass flow remains constant.

(4) Mass transfer does not change the volume of the drop.

(5) The volumetric flow rate of growth of the drop remains constant.

(6) The influence of satellite drops formed can be neglected.

(7) The mass transfer takes place across a plane into a

medium (continuous phase) having an area equivalent to that of the spherical drop.

(8) The drop is spherical throughout its history up to detachment.

Equation (24) has been used as a starting point by almost all the investigators for estimating mass transfer during drop formation. When this equation is applied to a single forming drop, obviously a term will have to be introduced for the changing area available for unsteady state mass transfer during drop formation. Thus, according to Higbie's penetration theory (16),

$$N'' = (c^* - c_o)\ A \left(\frac{D}{\pi t} \right)^{1/2} \qquad --- \quad (2{\cdot}6)$$

where N'' is the mass transferred per unit time across the exposed surface of a single drop, and may be appropriately termed as the "drop flux" (gm./sec.(single drop)) to differentiate it from the flux N' (gm./sec.cm.^{2}). The equations proposed by different investigators are based on different assumptions in averaging the area (A) and the duration for which this area is exposed to mass transfer. These equations have been brought to a common efficiency basis in the following paragraphs through the equation,

$$A = p t^q \qquad --- \quad (2{\cdot}7)$$

where the drop area is expressed as a function of time.

By combining Equations (2.6) and (2.7) Licht and Pansing (9) derived the equation,

$$N'' = (c^* - c_o)\, p \left(\frac{D}{\pi}\right)^{1/2} \cdot t^{\left(\frac{2q-1}{2}\right)} \qquad --- (2\cdot 8)$$

The total mass transfer (N) over time t can then be obtained from

$$N = \int_0^t N''\, dt \qquad --- (2\cdot 9)$$

which gives

$$N = \frac{2}{2q+1}\,(c^* - c_o)\, p \left(\frac{D}{\pi}\right)^{1/2} \cdot t^{\left(\frac{2q+1}{2}\right)} \qquad --- (2\cdot 10)$$

As pointed earlier, Popovic et al. (22) have used equations of the form represented by Equation (2.10) to compare the different models. Since the efficiency of mass transfer is a significant quantity, which expresses the approach of a mass transfer operation to equilibrium conditions, expressions are derived below for the efficiency of mass transfer during drop formation for the different models proposed.

The efficiency is given by

$$E = \frac{c_t - c_o}{c^* - c_o} \qquad --- \quad (2 \cdot 11)$$

By definition

$$\frac{N}{v} = (c_t - c_o) \qquad --- \quad (2 \cdot 12)$$

Substituting Equation (2.12) in (2.11),

$$E = \frac{N}{v\,(c^* - c_o)} \qquad --- \quad (2 \cdot 13)$$

Dividing both sides of Equation (2.10) by v, transferring (c^* - c_o) to the left hand side of the equation and then combining with Equation (2.13),

$$E = \frac{2}{2q+1} \cdot \frac{p}{v} \left(\frac{D}{\pi}\right)^{1/2} \cdot t^{\left(\frac{2q+1}{2}\right)} \qquad --- \quad (2 \cdot 14)$$

Baird (19) drew attention to the equation proposed by Ilkovic (18) and fully derived by MacGillavry and Rideal (23). The equation which was used to estimate the diffusion controlled current in a dropping-mercury cathode, is based on a model in which a sphere expands at a constant volume rate and the penetration depth is small compared with the sphere radius. In this equation it is assumed that resistance to diffusion is restricted to either of the phases. According to the Ilkovic model the drop flux during drop formation is given by

$$N'' = \left(\frac{7}{3}\right)^{1/2} (c^* - c_o) \left(\frac{D}{\pi}\right)^{1/2} \cdot \frac{A(t)}{t^{1/2}} \qquad --- (2\cdot15)$$

Substituting Equation (2.7) for area (A)

$$N'' = p \left(\frac{7}{3}\right)^{1/2} (c^* - c_o) \left(\frac{D}{\pi}\right)^{1/2} \cdot t^{\left(\frac{2q-1}{2}\right)} \qquad --- (2\cdot16)$$

The total mass transfer over a period t is then obtained from Equation (2.9)

$$N = \left(\frac{7}{3}\right)^{1/2} \frac{2}{2q+1} (c^* - c_o)\, p \left(\frac{D}{\pi}\right)^{1/2} \cdot t^{\left(\frac{2q+1}{2}\right)} \qquad --- (2\cdot17)$$

The efficiency of mass transfer is obtained by combining this equation with Equation (2.13)

$$E = \left(\frac{7}{3}\right)^{1/2} \cdot \frac{2}{2q+1} \cdot \frac{p}{v} \left(\frac{D}{\pi}\right)^{1/2} \cdot t^{\left(\frac{2q+1}{2}\right)} \qquad --- (2\cdot18)$$

Heertjes et al. (17) assumed that the velocity of diffusion is small compared to the velocity of drop growth and the time dependent area was averaged in the following manner.

$$N'' = (c^* - c_o)\left(\frac{D}{\pi}\right)^{1/2} \int_{\substack{A=0\\t=0}}^{\substack{A\\t}} \frac{dA}{t^{1/2}} \qquad --- \quad (2\cdot 19)$$

Differentiating Equation (2.7)

$$dA = qpt^{q-1} \qquad --- \quad (2\cdot 20)$$

Combining Equation (2.19) and (2.20)

$$N'' = (c^* - c_o)\; pq\left(\frac{D}{\pi}\right)^{1/2} \int_{t=0}^{t} t^{\left(\frac{2q-3}{2}\right)} \qquad --- \quad (2\cdot 21)$$

which on integration gives

$$N'' = \frac{2q}{2q-1}\;(c^* - c_o)\, p\left(\frac{D}{\pi}\right)^{1/2} t^{\left(\frac{2q-1}{2}\right)} \qquad --- \quad (2\cdot 22)$$

The total mass transfer up to time <u>t</u> is obtained by combining Equations (2.9) and (2.22) and integrating :

$$N = \frac{4q}{(4q^2-1)} (c^*-c_o)\, p \left(\frac{D}{\pi}\right)^{1/2} t^{\left(\frac{2q+1}{2}\right)} \qquad --- (2\cdot 23)$$

The efficiency of mass transfer can be obtained along lines similar to that for Equation (2.14)

$$E = \frac{4q}{4q^2-1} \cdot \frac{p}{v} \left(\frac{D}{\pi}\right)^{1/2} t^{\left(\frac{2q-1}{2}\right)} \qquad --- (2\cdot 24)$$

Coulson and Skinner (11) assumed that during the formation of a drop, the extraction takes place over the average area of the drop given by

$$A_{av.} = \int_o^t \frac{A\,dt}{t} \qquad --- (2\cdot 25)$$

which on combination with Equation (2.7) gives

$$A_{av.} = p\int_o^t t^{q-1}\,dt \qquad --- (2\cdot 26)$$

Then, from Equations (2.6) and (2.26),

$$N'' = (c^* - c_o)\, p \left(\frac{D}{\pi}\right)^{1/2} \frac{1}{t^{1/2}} \int_0^t t^{q-1}\, dt \qquad \text{--- } (2{\cdot}27)$$

which on integration gives

$$N'' = (c^* - c_o)\, \frac{p}{q} \left(\frac{D}{\pi}\right)^{1/2} t^{\left(\frac{2q-1}{2}\right)} \qquad \text{--- } (2{\cdot}28)$$

By methods similar to those described earlier, the following equations can be obtained for N and E :

$$N = \frac{2}{2q+1} (c^* - c_o)\, \frac{p}{q} \left(\frac{D}{\pi}\right)^{1/2} t^{\left(\frac{2q+1}{2}\right)} \qquad \text{--- } (2{\cdot}29)$$

$$E = \frac{2}{2q+1} \cdot \frac{p}{q} \cdot \frac{1}{v} \left(\frac{D}{\pi}\right)^{1/2} t^{\left(\frac{2q+1}{2}\right)} \qquad \text{--- } (2{\cdot}30)$$

Groothuis and Kramers (14) have argued that the mass transfer should depend on the duration for which the surface is exposed for the diffusion of the solute from one phase to the other. In other words, any area increase during the growth of a drop produces fresh surface and there is no mixing between areas of different ages. If any area dA is formed at time, $\underline{t}$, the rate of mass transfer throughout that area at any time t_1 (where $t \angle t_1 \angle t_f$) is given by

$$N'' = (c^* - c_o)\left(\frac{D}{\pi}\right)^{1/2} \frac{dA}{(t_1 - t)^{1/2}} \qquad --- \quad (2\cdot31)$$

Expressing dA in terms of Equation (2.20)

$$N'' = (c^* - c_o)\, q\, p \left(\frac{D}{\pi}\right)^{1/2} \int_0^{t_1} \frac{t^{q-1}\, dt}{t^{1/2}(1 - {}^{t}/_{t_1})} \qquad --- \quad (2\cdot32)$$

This equation can be put in the form,

$$N'' = 2\int_0^1 (1-y^2)^{q-1}\, dy \cdot (c^* - c_o)\, q\, p \left(\frac{D}{\pi}\right)^{1/2} t^{\left(\frac{2q-1}{2}\right)} \qquad --- \quad (2\cdot33)$$

where

$$\left.\begin{aligned} y &= (1 - {}^{t}/_{t_1})^{1/2} \\ t^{q-1} &= (1 - y^2)^{q-1}\, t_1^{\,q-1} \\ dt &= -2 y t_1\, dy \end{aligned}\right\} \qquad --- \quad (2\cdot34)$$

In this equation t_1 represents the drop formation time for one set of experiments and is therefore a constant.

For a constant value of q the integral

$$\int_0^1 (1-y^2)^{q-1}\,dy$$

is a constant. Taking t_1 as a variable and integrating Equation (2.33) and writing t instead of t_1, the corresponding total mass transfer may be obtained.

$$N = \frac{4q}{2q+1}\int_0^1 (1-y^2)^{q-1}\,dy\,(c^*-c_o)\,p\left(\frac{D}{\pi}\right)^{1/2} t^{\left(\frac{2q+1}{2}\right)} \qquad \text{---}\ (2\cdot35)$$

The efficiency of extraction is then given by

$$E = \frac{4q}{2q+1}\int_0^1 (1-y^2)^{q-1}\,dy\cdot\frac{p}{v}\left(\frac{D}{\pi}\right)^{1/2} t^{\left(\frac{2q+1}{2}\right)} \qquad \text{---}\ (2\cdot36)$$

Two different mechanisms of mass transfer to a growing drop were examined by Heertjes and Denie (26). The first mechanism is based on stretching of the surface - the interfacial film is assumed to be uniformly stretched over the drop surface as the drop grows. The second mechanism describes the growth of a drop by additions of fresh elements to the surface.

The theory for the first mechanism is based on the work of Ilkovic (18) and extended by MacGillavry and Rideal (23). Baird (19) and Beek and Kramers (27) have drawn attention to this mechanism. The efficiency was defined for the continuously forming drop (by neglecting the so-called rest drop) as

$$E_{\substack{\text{STRETCHING}\\ \text{THEORY}}} = \left(\frac{7}{3}\right)^{1/2} \cdot \frac{2}{\pi^{1/2}} \left(\frac{Dt_f}{r_f^2}\right)^{1/2} \qquad \text{--- (2·37)}$$

The theory for the second mechanism is based on that given by Heertjes et al. (17), and Sawistowski and Goltz (28), and the time of contact defined by Groothuis and Kramers (14) has been retained. The efficiency for the continuously forming drop (neglecting the rest drop part) again was defined as

$$E_{\substack{\text{SURFACE}\\ \text{RENEVAL}\\ \text{THEORY}}} = \frac{4}{\pi^{1/2}} \left(\frac{Dt_f}{r_f^2}\right)^{1/2} \qquad \text{--- (2·38)}$$

In another model, Michels'(25), it was assumed that bubble growth was spherical with its centre moving. The volumetric rate growth was constant producing radial motion in the continuous phase. The drop growth was not accompanied by tangential motion of its surface. The diffusion layer was assumed to be stretched by the moving interface, the biggest stretching occurring at the front of the spheres and the smallest at the rear. The following equation for N was developed

$$N = \frac{16 \cdot \pi}{6} \cdot \left(\frac{3}{4\pi}\right)^{7/6} (7 + 6 \cos \omega')^{1/2} (c^{*} - c_0)\, 4\, (D\pi)^{1/2}\, r_f^{2}\, t_f^{-2/3}\, t^{7/6} \qquad \text{--- (2.39)}$$

If N has to be measured over a time interval t_f, then $t = t_f$. Making this change in Equation (2.39) and rewriting it in terms of efficiency

$$E = 0.495\, (7 + 6 \cos \omega')^{1/2}\, \frac{4}{v} (D\pi)^{1/2}\, r_f^{2}\, t_f^{1/2} \qquad \text{--- (2.40)}$$

which, after simplification gives

$$E = 0.495\, (7 + 6 \cos \omega')^{1/2}\, \frac{3}{\pi^{1/2}} \left(\frac{D t_f}{r_f^{2}}\right)^{1/2} \qquad \text{--- (2.41)}$$

where

$\cos \omega' = 1$ for the front of the bubble

$\cos \omega' = 0$ for the equator of the bubble

$\cos \omega' = -1$ for the reat of the bubble

The value of E will obviously vary with the region of the bubble considered.

2.2 GENERALIZED EQUATION FOR EFFICIENCY

The different equations for the efficiency of mass transfer derived in the previous section can be put in a single generalized form. The constants of these equations will be different for the different models proposed. A meaningful comparison of the models can then be made from the magnitudes of these constants.

Equations (2.14), (2.18), (2.24), (2.30) and (2.36) can be written as

$$E = \alpha_1 \frac{p}{v} \left(\frac{D}{\pi}\right)^{1/2} t^{\left(\frac{2q+1}{2}\right)} \qquad --- (2.42)$$

in which p and q can be evaluated as follows.

Since the volumetric rate of growth of the drops is constant, and since it is assumed that the drop is spherical throughout its history up to detachment,

$$\frac{dv}{dt} = C \qquad --- \quad (2\cdot 43)$$

since

$$v = (4\pi r^2)^{3/2} \ (4\pi)^{-3/2} \cdot \frac{4\pi}{3}$$

and

$$v = C_1 \cdot A^{3/2} \qquad --- \quad (2\cdot 44)$$

where C and C_1 are constants.

From Equations (2.43) and (2.44)

$$\frac{dv}{dt} = C_1 \frac{d}{dt} (A^{3/2}) = C$$

$$\int d\,(A^{3/2}) = C_2 \int dt \qquad --- \quad (2\cdot 45)$$

By integrating Equation (2.45) and rearranging

$$A = C_3 \ t^{2/3} \qquad --- \quad (2\cdot 46)$$

Comparing this equation with Equation (2.7)

$$q = \frac{2}{3}$$

and

$$p = 4\pi\, r_f^2\, t_f^{-2/3} \qquad --- \quad (2\cdot 47)$$

where $A = 4\pi\, r_f^2$

Substituting for p, q and v, Equation (2.42) becomes

$$E = 3\alpha_1 \left(\frac{D}{\pi}\right)^{1/2} r^{-1}\, t^{-2/3}\, t^{7/6} \qquad --- \quad (2\cdot 48)$$

Equation (2.48) expresses E as a function of any time instant t and the drop formation time t_f. If E has to be measured over a time interval of t_f then $t = t_f$ and Equation (2.48) becomes

$$E = \alpha_1\, \frac{3}{\pi^{1/2}} \left(\frac{D t_f}{r_f^2}\right)^{1/2} \qquad --- \quad (2\cdot 49)$$

which on simplification gives

$$E = \alpha_2 \left(\frac{D t_f}{r_f^2}\right)^{1/2} \qquad --- \quad (2\cdot 50)$$

where

$$\alpha_2 = \frac{3}{\pi^{1/2}}\, \alpha_1 \qquad --- \quad (2\cdot 51)$$

The values of α_2 for the different models are summarized in Table (2.1).

TABLE (2.1)

VALUES OF THE CONSTANT α_2 FOR THE DIFFERENT MODELS PROPOSED

Authors	α_2	Reference
Licht and Pansing	1.451	(9)
Ilkovic	2.215	(18)
Heertjes, Holve and Talsma	5.803	(17)
Coulson and Skinner	2.175	(11)
Groothuis and Kramers	2.570	(14)
Heertjes and Denie		
1) Surface stretching theory	1.692	(26)
2) Surface renewal theory	2.275	
Michels		
Cos $\omega' = 1$	3.030	(25)
Cos $\omega' = 0$	2.220	
Cos $\omega' = -1$	0.832	
Haritatos and Liberman	2.495	(24)
Least squares value from the present work.*	5.142	

* This is presented and discussed in Chapter - 6.

CHAPTER – 3

HYDRODYNAMICS OF DROP GROWTH

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HYDRODYNAMICS OF DROP GROWTH

In this chapter a theory is developed for the hydrodynamics of drop growth based on an analogy between Maxwell's electromagnetic field equations and Euler's equations for incompressible fluids. Using this similarity the stream function of the growing drop is determined. This information is subsequently made use of in the next chapter for predicting the mass transfer coefficient.

3.1 KINEMATIC SIMILARITY BETWEEN THE MAXWELL AND EULER EQUATIONS

The problem of mass transfer to and from a spherical drop of liquid (A) injected through a submerged nozzle into a continuous phase (B) - immiscible with (A) - requires for its solution as a first step, complete knowledge of the velocity distribution (internal circulation) inside the spherical drop (A). The internal circulation can be readily seen to be ascribable to

(1) the finite injection velocity at the nozzle;

(2) the tangential viscous drag all along the interface between the liquid drop (A) and the continuous phase

(B), through which the drop is made to rise with an appreciable velocity which varies in the course of drop formation.

The exact hydrodynamical treatment of the non-stationary boundary value problem comprising both the mechanisms listed above is extremely difficult, primarily because of the changing boundary condition (varying drop diameter), and also because of the complexity of the geometric considerations attending the submerged nozzle. It is possible, however, to arrive at a reasonable solution in a closed form under certain simplifying assumptions. The streamline pattern due to the viscous drag can, for instance, be calculated by assuming the drop to have an average diameter and rise through the continuous phase with an average velocity, both of which can be computed in terms of time of formation and injection rate, and directly using the Hadamard-Rybczinski solution (29, 31). Averaging, of course, is to be done with a weighting factor appropriate to the problem.

For reasons which will be made clear in the text to follow, the contribution to the total internal circulation induced by the viscous drag (Hadamard-Rybczinski mechanism) is relatively small for the problem on hand, and hence we are led to consider the internal circulation caused by the finite injection velocity. A semi-phenomenological treatment of the latter can be given on the following lines. At the very outset, it may be noted that while viscosity (of both continuous and dispersed phases) enters the Hadamard-Rybczinski scheme in an essential way since it is exclusively responsible for the induced circulation, it appears in the present mechanism only as a dissipative factor, and as such can be neglected in the first approximation. This amounts to assuming the liquids to be ideal, and regarding the continuous phase as merely providing containment. As regards the changing boundary condition, i.e. the varying drop diameter, it is not possible to assume an average drop diameter (as could be done in the case of the Hadamard-Rybczinski mechanism) because of its incompatibility with the incompressibility of the liquid (A) injected at a non-zero rate through the nozzle. One can, however, and this is crucial to the present treatment, make use of the mathematical artifice of adiabatic stepwise solution, in which one solves the problem of flow for an instantaneous boundary condition, i.e. instantaneous drop diameter, and then allows the boundary condition (drop diameter) to vary with time as a parameter. This artifice is justified if the total time of formation is large compared with the characteristic time of circulation.

In the following, a semi-phenomenological solution of the problem of internal circulation for the given injection velocity is obtained under the above mentioned simplifying assumptions. In order to do this, use is made of a striking kinematic analogy which exists between the present problem and a certain electromagnetic problem having a well known solution. It is observed that the streamline pattern inside the drop is similar to the magnetic lines of force in a lossless microwave cavity (spherical) oscillating in TE_{101} mode - the dominant mode. The essential nature of the kinematic analogy can be best understood in terms of the similarity of the differential equations and the boundary conditions governing the two analogues, namely the Maxwell field equations of electromagnetism and Euler's field equations of hydrodynamics. The two sets of equations can be summarized for later reference and completeness as follows. The electromagnetic field is completely defined in terms of the field quantities, $\vec{E}$, $\vec{B}$, $\vec{D}$, $\vec{H}$, and current sources, $\vec{J}$, and charges, ρ , which satisfy the vector differential equations

$$\mathrm{curl}\ \vec{E} = -\frac{\partial \vec{B}}{\partial t} \qquad --- (3\cdot1)$$

$$\mathrm{curl}\ \vec{H} = \vec{J} + \frac{\partial \vec{D}}{\partial t} \qquad --- (3\cdot2)$$

$$\mathrm{div}\ \vec{B} = 0 \qquad --- (3\cdot3)$$

$$\mathrm{div}\ \vec{D} = \rho \qquad --- (3\cdot4)$$

and in a homogeneous isotropic medium we have the additional relations

$$\vec{D} = K\vec{E} \qquad \text{---} \quad (3\cdot5)$$

$$\vec{B} = \mu\vec{H} \qquad \text{---} \quad (3\cdot6)$$

$$\vec{J} = \sigma\vec{E} \qquad \text{---} \quad (3\cdot7)$$

In the rationalised MKS system of units we have,

$\vec{E}$ = electric intensity, volts per m.

$\vec{B}$ = magnetic induction, webers per m.

$\vec{D}$ = electric displacement, coulombs per m^2.

$\vec{H}$ = magnetic intensity, amp. per m.

$\vec{J}$ = current density, amp. per m^2.

σ = electric conductivity, 1/ohm-m.

K = $K_r K_o$ = electric inductive capacity of medium

μ = $\mu_r \mu_o$ = magnetic inductive capacity of medium

K_r = dielectric constant

μ_r = permeability

K_o = 8.854×10^{-12} farad per m.

μ_o = $4\pi \times 10^{-7} = 1.257 \times 10^{-6}$ henry per m

ρ = charge density, coulombs per m^2.

C'' = $1/\sqrt{K_o \mu_o} = 2.998 \times 10^{8}$ m. per sec.

In addition one has the continuity equations indicating charge conservation

$$\frac{\partial \rho}{\partial t} + \operatorname{div} \vec{J} = 0 \qquad \text{---} \quad (3\cdot8)$$

For the solution of an electromagnetic problem, the above equations are to be supplemented by boundary conditions appropriate to the problem.

Euler's equations of hydrodynamics of incompressible, ideal fluid flow can be expressed in terms of the field quantities, $\vec{V}$, P, and the fluid density ρ as,

$$\frac{\partial \vec{V}}{\partial t} + (\vec{V}\,\mathrm{grad})\,\vec{V} = -\frac{1}{\rho}\,\mathrm{grad}\;P \qquad --- \quad (3\cdot 9)$$

or in its equivalent form,

$$\frac{\partial}{\partial t}\,(\mathrm{curl}\;\vec{V}) = \mathrm{curl}\,(\vec{V} \times \mathrm{curl}\;\vec{V}) \qquad ---(3\cdot 10)$$

In stationary state (no change with time)

$$\frac{\partial}{\partial t} \equiv 0$$

Thus, Equation (3 · 10) reduces to

$$\mathrm{curl}\,(\vec{V} \times \mathrm{curl}\;\vec{V}) = 0 \qquad ---(3\cdot 11)$$

and the continuity equation,

$$\frac{\partial \rho}{\partial t} + div\,(\rho \vec{V}) = 0 \qquad --- \quad (3\cdot12)$$

reduces to

$$div\ \vec{V} = 0 \qquad --- \quad (3\cdot13)$$

For an incompressible fluid (i.e. constant ρ) the above equations, together with the appropriate boundary conditions, completely define the flow.

The kinematic analogy of interest is formally based on the realisation that the field quantities, $\vec{V}$ and $\vec{H}$, both satisfy very similar differential equations and, of course, satisfy exactly the same boundary conditions.

In the first place it is noted that :

$$\text{div}\ \vec{V} = 0 \qquad (3.14)$$

$$\text{div}\ \vec{H} = 0 \qquad (3.15)$$

and the boundary conditions

$$\vec{n}\,.\,\vec{V} = 0$$

$$\vec{n}\,.\,\vec{H} = 0$$

where $\vec{n}$ is the unit vector normal to the bounding surface, which in the case of a spherical drop is the interfacial surface; while in the case of a microwave cavity, the perfectly conducting wall. Further we have from Maxwell's equation

$$\text{curl}\ \vec{H} = \epsilon \frac{\partial \vec{E}}{\partial t} + \vec{J}$$

when there is no current inside the cavity, $\vec{J} = 0$. Thus,

$$\text{curl}\ \vec{H} = \epsilon \frac{\partial \vec{E}}{\partial t} \qquad \text{---} \quad (3\cdot 16)$$

Taking the cross product on both sides with $\vec{H}$ and then taking curl we get,

$$\begin{aligned}\text{curl}\ (\vec{H} \times \text{curl}\ \vec{H}) &= \epsilon\ \text{curl}\ (\vec{H} \times \frac{\partial \vec{E}}{\partial t}) \\ &= i\ \omega\ \epsilon\ \text{curl}\ (\vec{H} \times \vec{E}) \qquad \text{---} \quad (3\cdot 17)\end{aligned}$$

where ω is the circular frequency of the field oscillations assumed to be cisoidal. The right hand side of Equation (3.17) has a time average zero for fields bounded in space as in the case of the spherical cavity. This follows from the fact that for electromagnetic fields bounded in space, the vectors, $\vec{E}$ and $\vec{H}$, are in quadrature, i.e. have a relative phase lag of $\pi/2$. This permits us to rewrite Equation (3.16) in an averaged sense as,

$$\mathrm{curl}\,(\vec{H} \times \mathrm{curl}\,\vec{H}) = 0 \qquad \text{---} \quad (3\cdot 18)$$

which is exactly the same as Equation (3.11) if we replace $\vec{H}$ by $\vec{V}$. Still another way of arriving at Equation (3.18) would be to take the low frequency limit of Equation (3.17). The above treatment establishes the kinematic similarity of the two problems. This permits us to solve the problem on hand in terms of its electromagnetic analogue (spherical microwave cavity in the dominant mode) by making the following identifications:

	Electromagnetic	Hydrodynamic	
1)	$\vec{H}$ (magnetic field)	$\vec{V}$ (velocity)	
2)	Magnetic lines of force	Streamlines	
3)	div $\vec{H} = 0$	div $\vec{V} = 0$	(3.19)

Boundary condition :

Radial component

$\vec{H}_r = 0$	$\vec{V}_r = 0$	(3.20)
at $r = a$	at $r = a$	

The kinematic analogy arrived at in the foregoing section must not be taken too literally. In point of fact, the electromagnetic analogue (the spherical microwave cavity) admits of infinite number of modes as solution, while in the case of internal circulation in the drop in question it is only the TE_{101}-like streamline pattern which is pertinent. It is believed that the analogy is fairly exact for this dominant mode. Dynamically, the two problems are completely dissimilar in that the inertia-force relations are different. However, in both the cases the trajectory of a descriptive point can be expressed in parametric form involving space co-ordinates only, which are similar in the two cases. This in itself ensures a geometric similarity between the two analogues. The physical plausibility of the above kinematic similarity for TE_{101}-like mode is self-evident.

3.2 VELOCITY DISTRIBUTION INSIDE THE DROP

Based on the previous analogy, $\vec{V} = \vec{H}$, one can arrive at the velocity distribution in the drop by solving Maxwell's equations for TE_{101} mode, inside a spherical lossless cavity with perfectly conducting walls.

The axially symmetric TE-modes can be obtained in the usual spherical co-ordinate systems as (30) :

$$E_{\phi} = \frac{B_n}{r^{1/2}} P_n^1 (\cos \theta) \, Z_{n+1/2}(Kr) \qquad --- (3\cdot 21)$$

$$H_\theta = -\frac{B_n P_n^1(\cos\theta)}{j\omega\mu r^{3/2}}\left[nZ_{n+\frac{1}{2}}(Kr) - KrZ_{n-\frac{1}{2}}(Kr)\right] \quad \text{---} \ (3\cdot 22)$$

$$H_r = \frac{B_n n Z_{n+\frac{1}{2}}(Kr)}{j\omega\mu r^{3/2}(\sin\theta)}\left[\cos\theta\, P_n^1(\cos\theta) - P_{n+1}^1(\cos\theta)\right] \quad \text{---} \ (3\cdot 23)$$

where $Z_{n+\frac{1}{2}}$ is half integral Bessel function; $P_n^1(\cos\theta)$, the Legendre function of first kind of order n. B_n, K, ω are certain constants which will be eliminated.

For the TE_{101} mode (the dominant mode) n = 1; one thus obtains

$$E_\phi = \frac{C'\sin\theta}{Kr}\left(\frac{\sin Kr}{Kr} - \cos Kr\right) \quad \text{---} \ (3\cdot 24)$$

$$H_r = \frac{2j\eta C'\cos\theta}{Kr}\left(\frac{\sin Kr}{Kr} - \cos Kr\right) \quad \text{---} \ (3\cdot 25)$$

$$H_\theta = \frac{j\eta C'\sin\theta}{K^2r^2}\left(\frac{(Kr)^2-1}{Kr}\sin Kr + \cos Kr\right) \quad \text{---} \ (3\cdot 26)$$

where K is given by the boundary condition,

$$H_{r=a} = 0$$

or

$$\operatorname{tg} Ka = Ka \qquad (3.27)$$

the principal solution being $Ka = 4.5$, where a is the radius of the sphere.

The constant, $j\eta C'$, can be evaluated in terms of the value of $\vec{H}$ at the centre, r = 0.

From Equation (3.25), one obtains for the field H_o at the centre (r = 0)

$$H_o \equiv \lim_{\substack{\theta = 0 \\ r \to 0}} H_r = 2\, j\eta C' \, \frac{\left(\dfrac{\sin Kr}{Kr} - \cos Kr\right)}{K^2 r^2}$$

or

$$H_o = j\eta C' \qquad --- \quad (3\cdot 28)$$

Equations (3.25) and (3.26) can now be rewritten as

$$H_r = \frac{2H_o \cos\theta}{K^2 r^2}\left(\frac{\sin Kr}{Kr} - \cos Kr\right) \qquad --- \quad (3\cdot 29)$$

$$H_\theta = -\frac{H_o \sin\theta}{K^2 r^2}\left(\frac{(Kr)^2 - 1}{Kr}\sin Kr + \cos Kr\right) \qquad --- \quad (3\cdot 30)$$

$$H_\phi = 0 \qquad --- \quad (3\cdot 31)$$

Hence, replacing $\vec{H}$ by $\vec{V}$ everywhere, the radial and tangential components of velocity at any point (r, θ) can be obtained as,

$$V_{r(r,\theta)} = \frac{2V_o \cos\theta}{K^2 r^2}\left(\frac{\sin Kr}{Kr} - \cos Kr\right) \qquad ---(3\cdot 32)$$

$$V_{\theta\,(r,\theta)} = -\frac{V_o \sin\theta}{K^2 r^2}\left(\frac{(Kr)^2-1}{Kr}\sin Kr + \cos Kr\right) \qquad ---(3\cdot 33)$$

$$V_\phi = 0 \qquad ---(3\cdot 34)$$

where K is given by Equation (3.27).

3.3 DETERMINATION OF CENTRE OF CIRCULATION

From the streamline configuration corresponding to TE_{101} mode, it can be seen that the locus of the centres of circulation is a circle which lies in the equatorial plane

$$\theta = \pi/2$$

and has a radius, r_c. The latter can be determined from the condition that

$V_r = 0$

$V = 0$

at $r = r_c$, radial distance of centre of circulation. One gets,

$$V_{r(r,\theta)} = \frac{2V_o \cos \pi/2}{K^2 r_c^2}\left(\frac{\sin Kr_c}{Kr_c} - \cos Kr_c\right) = 0 \qquad ---(3\cdot 35)$$

$$V_{\theta\,(r,\theta)} = -\frac{V_o \sin \pi/2}{K^2 r_c^2} \left(\frac{(Kr_c)^2 - 1}{Kr_c} \sin Kr_c + \cos Kr_c \right) = 0 \qquad \text{--- (3.36)}$$

Equation (3.35) is identically satisfied for all r_c as $\cos \pi/2 = 0$. Equation (3.36) gives

$$\left(\frac{(Kr_c)^2 - 1}{Kr_c} \sin Kr_c + \cos Kr_c \right) = 0 \qquad \text{--- (3.37)}$$

and

$$tg\, Kr_c = \frac{Kr_c}{1 - (Kr_c)^2} \qquad \text{--- (3.38)}$$

having the principal solution

$$Kr_c = 2{\cdot}74 \qquad \text{--- (3.39)}$$

k is given by Equation (3.27)

$$K = \frac{4{\cdot}5}{a} \qquad \text{--- (3.40)}$$

Substituting Equation (3.40) in Equation (3.39) r_c can be obtained

$$r_c = 0{\cdot}609\,a \qquad \text{--- (3.41)}$$

The theoretical determination of the centre of circulation based on the foregoing model derives excellent support from the experimental findings of Heertjes et al. (17). In order to separate the contribution of mass transfer during drop formation from that taking place during coalescence, they formed the drop one mm. above the liquid surface, and using a photographic technique observed that in some cases a small bubble of air was trapped in the drop. From photographic analysis it was found that the entrapped air bubble was always stagnant in the equatorial plane and the maximum distance of this bubble from the centre of the drop was found to be 0.6a where a is the radius of the drop.

Now, from general principles of mechanics, the minimum potential energy state is the one favoured by the system left to itself. For a given total energy, partly kinetic and partly potential, the minimum potential energy corresponds to the maximum kinetic energy. For an inhomogeneous system having species of two different densities the above consideration forces the denser of the two towards the region of higher velocity and conversely the lighter towards the region of lower velocity. In the experiments referred to above the air bubble corresponds to the lighter of the two components, and is accordingly forced towards the region of minimum velocity, which in this case corresponds to the centre of circulation. One is, therefore, led to the conclusion that the air bubble trapped must come to rest at the centre of circulation which is at 0.6 a from the centre in the equitorial plane. The above phenomenon is, in fact, only a manifestation of the virial theorem of Clausius.

In the light of the foregoing reasoning, the agreement between the theoretical prediction based on the proposed model and the experimental evidence as to the location of centre of circulation justifies the correctness of the model.

In this connection it may be recalled that the centre of circulation, as obtained by Hadamard-Rybczinski (29, 31) by solving the boundary value problem for a spherical drop falling through an immiscible continuous medium, is 0.71a from the centre. In this model, however, the internal circulation was assumed to be set up exclusively by the viscous drag all along the interface, while in the present analysis the internal circulation has been attributed to the injection velocity at the nozzle.

3.4 DETERMINATION OF THE STREAM FUNCTION ψ

To complete the hydrodynamics of internal circulation in the drop, we proceed to determine the stream function, which is subsequently needed for computing the average time of circulation. The stream function is related to the radial and tangential velocity components, V_r , V_θ, by the following differential equations,

$$V_{\theta(r,\theta)} = -\frac{1}{r\sin\theta}\cdot\frac{\partial\psi}{\partial r} \qquad --- \quad (3\cdot 42)$$

$$V_{r(r,\theta)} = \frac{1}{r^2\sin\theta}\cdot\frac{\partial\psi}{\partial\theta} \qquad --- \quad (3\cdot 43)$$

where

$$V_{\theta(r,\theta)} = \frac{V_0\sin\theta}{\left(\frac{4\cdot 5}{a}r\right)^2}\left[\frac{\left(\frac{4\cdot 5}{a}r\right)^2-1}{\frac{4\cdot 5}{a}r}\sin\frac{4\cdot 5}{a}r+\cos\frac{4\cdot 5}{a}r\right] \qquad --- \quad (3\cdot 44)$$

$$V_{r(r,\theta)} = \frac{2V_0\sin\theta}{\left(\frac{4\cdot 5}{a}r\right)^2}\left[\frac{\sin\frac{4\cdot 5}{a}r}{\frac{4\cdot 5}{a}r}-\cos\frac{4\cdot 5}{a}r\right] \qquad --- \quad (3\cdot 45)$$

Following Fourier method of separation of variables, and noting that there is no ϕ variation,

$$\psi_{(r,\theta)} = R(r)\,\Theta(\theta) \qquad --- \quad (3\cdot 46)$$

Substituting in Equation (3.43),

$$V_{r(r,\theta)} =$$

$$\frac{1}{r^2}\cdot\frac{1}{\sin\theta}R(r)\frac{\partial\Theta}{\partial\theta} = \frac{2V_0\cos\theta}{\left(\frac{4\cdot 5}{a}r\right)^2}\left[\frac{\sin\frac{4\cdot 5}{a}r}{\frac{4\cdot 5}{a}r}-\cos\frac{4\cdot 5}{a}r\right]$$

$$--- \quad (3\cdot 47)$$

Equating the Θ part of Equation (3.47)

$$\frac{1}{\sin\theta}\cdot\frac{\partial\Theta}{\partial\theta} = 2\cos\theta$$

$$\partial\Theta = 2\cos\theta\,\sin\theta\,\partial\theta$$

$$\Theta_{(\theta)} = \sin^2\theta \qquad \text{--- (3.48)}$$

Equating the radial part of Equation (3.47)

$$\frac{1}{r^2}R(r) = \frac{V_0}{\left(\frac{4.5}{a}\right)^2 r^2}\left[\frac{\sin\frac{4.5}{a}r}{\frac{4.5}{a}r} - \cos\frac{4.5}{a}r\right]$$

$$R(r) = \frac{V_0}{\left(\frac{4.5}{a}\right)^2}\left[\frac{\sin\frac{4.5}{a}r}{\frac{4.5}{a}r} - \cos\frac{4.5}{a}r\right] \qquad \text{--- (3.49)}$$

On substituting Equations (3.48), (3.49), (3.46) the stream function reduces to

$$\psi_{(r,\theta)} = \frac{V_0\sin^2\theta}{\left(\frac{4.5}{a}\right)^2}\left[\frac{\sin\frac{4.5}{a}r}{\frac{4.5}{a}r} - \cos\frac{4.5}{a}r\right] \qquad \text{--- (3.50)}$$

It can be easily verified that the stream function (3.50) satisfies the other equation [(3.44)] and the solution is therefore consistent.

The different streamlines are given by the parametric equation

$$\psi_{(r,\theta)} = C \qquad \text{--- (3.51)}$$

and lie in the meridional plane, where C ranges between C_{max} and C_{min}. The bounds, C_{max} and C_{min}, can be arrived at from the following considerations. C decreases monotonically from C_{max}, corresponding to the vanishing streamline at the centre of circulation, to C_{min}, corresponding the outermost streamline describing a semi-circle. The streamline distribution in the drop for different values of C is shown in Fig. (3.1).

Determination of C_{min} and C_{max}

C_{min} can be determined directly from the fact that the outermost streamline has as its part the radial line $\theta = 0$ and hence from Equation (3.50), the corresponding value of C is equal to zero,

$$C_{min} = 0 \qquad \text{--- (3.52)}$$

C_{max} can be determined by maximizing C with respect to θ and r ; accordingly we put $\theta = \pi/2$ and obtain the conditions

$$\frac{\partial C}{\partial r} = \frac{\partial}{\partial r}\left[\frac{\sin \frac{4\cdot 5}{a} r}{\frac{4\cdot 5}{a} r} - \cos \frac{4\cdot 5}{a} r\right] = 0 \qquad \text{--- (3.53)}$$

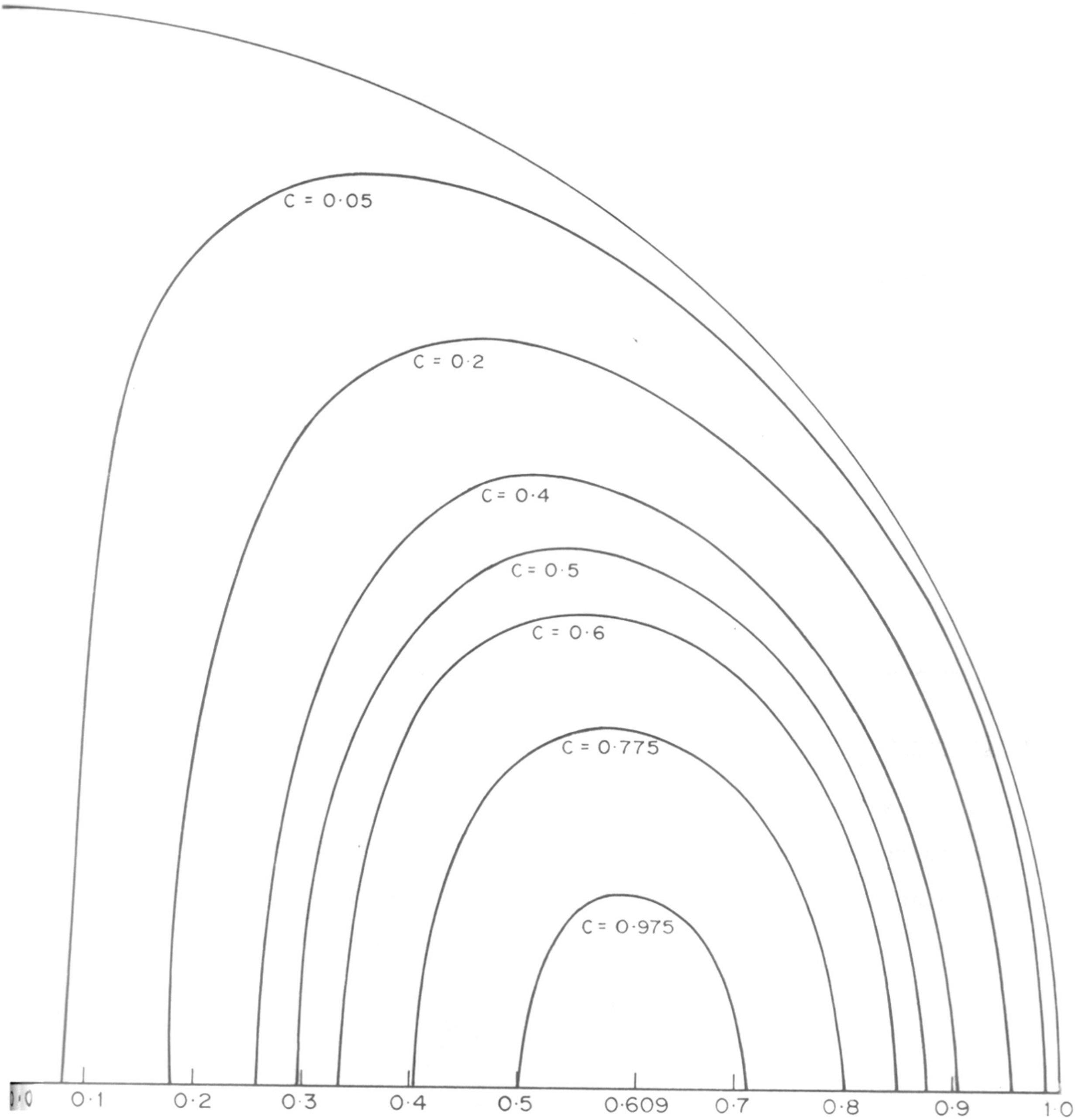


FIG.(3·1). INSTANTANEOUS STREAMLINE PROFILES IN A GROWING DROP.

$$\frac{\partial C}{\partial r} = -\frac{1}{r}\left[\frac{\left(\frac{4\cdot5}{a}r\right)^2-1}{\frac{4\cdot5}{a}r}\sin\frac{4\cdot5}{a}r+\cos\frac{4\cdot5}{a}r\right] \qquad \text{--(3.54)}$$

Equation (3.54) is solved to yield r = 0.609a which coincides with the centre of circulation; the corresponding value of C_{max} is

$$C_{max} = \frac{V_o}{\left(\frac{4\cdot5}{a}\right)^2}\left[\frac{\sin 2\cdot73}{2\cdot73} - \cos 2\cdot73\right]$$

$$C_{max} = \frac{1\cdot063}{4\cdot5^2} V_o a^2$$

$$C_{max} = 0\cdot0525 \; V_o a^2$$

$$0 \leq C \leq 0\cdot0525 \; V_o a^2 \qquad \text{---} \; (3\cdot55)$$

3.5 EVALUATION OF THE TIME OF CIRCULATION OVER THE STREAMLINE

Determination of the effective mass transfer coefficient involves an expression for the average time of circulation for the streamlines. The time of circulation along a streamline defined by Equation (3.51),

$$\psi_{(r,\theta)} = C$$

is given by

$$t_c = \oint \frac{ds}{V} \qquad \text{---} \; (3\cdot56)$$

where ds is a line element along the prescribed streamline,

$$ds = \left[(dr)^2 + (r\,d\theta)^2\right]^{1/2} \qquad ---(3{\cdot}57)$$

and $V_{(r,\theta)}$ is a velocity at the point,

$$V_{(r,\theta)} = \left[V^2_{r(r,\theta)} + V^2_{\theta(r,\theta)}\right]^{1/2} \qquad ---(3{\cdot}58)$$

where $V_{r(r,\theta)}$ and $V_{\theta(r,\theta)}$ are given by Equation (3.32) and (3.33).

The expression could be put in a convenient form in terms of normalised variables as follows. Putting,

$$x = Kr = \frac{4{\cdot}5}{a}r \qquad ---(3{\cdot}59)$$

in the expressions for V_r and V_θ one obtains

$$\psi_{(x,\theta)} \equiv \frac{\psi_{(r,\theta)}}{V_o}\left(\frac{4{\cdot}5}{a}\right)^2 \qquad ---(3{\cdot}60)$$

$$\psi_{(x,\theta)} = \sin^2\theta\left[\frac{\sin x}{x} - \cos x\right] = C \qquad ---(3{\cdot}61)$$

where $\psi_{(x,\theta)}$ is a normalised stream function and

$$0 \leq C \leq 1{\cdot}063$$

Normalised velocity components are given by

$$v'_{r(x,\theta)} \equiv \frac{V_{r(r,\theta)}}{V_o} = \frac{2\cos\theta}{x^2}\left[\frac{\sin x}{x} - \cos x\right] \quad \text{---}(3{\cdot}62)$$

$$v'_{\theta(x,\theta)} \equiv \frac{V_{\theta(r,\theta)}}{V_o} = -\frac{\sin\theta}{x^2}\left[\frac{x^2-1}{x}\sin x + \cos x\right] \quad \text{---}(3{\cdot}63)$$

also for the line element

$$ds = \frac{a}{4{\cdot}5}\left[(dx)^2 + (x\,d\theta)^2\right]^{1/2} \quad \text{---}(3{\cdot}64)$$

From the above can be obtained

$$V = V_o\left[v'^{\,2}_{r(x,\theta)} + v'^{\,2}_{\theta(x,\theta)}\right]^{1/2} \quad \text{---}(3{\cdot}65)$$

the time of circulation t_c reduces to

$$t_c = \oint \frac{1}{V_o}\cdot\frac{a}{4{\cdot}5}\,\frac{\left[(dx)^2 + (x\,d\theta)^2\right]^{1/2}}{\left[v'^{\,2}_{r(x,\theta)} + v'^{\,2}_{\theta(x,\theta)}\right]^{1/2}} \quad \text{---}(3{\cdot}66)$$

or

$$t_c \equiv \frac{d}{V_o}\,\alpha_c \qquad \text{--- (3.67)}$$

with

$$\alpha_c = \oint \frac{1}{9} \cdot \frac{\left[(dx)^2 + (x\,d\theta)^2\right]^{1/2}}{\left[v'^{\,2}_{r(x,\theta)} + v'^{\,2}_{\theta(x,\theta)}\right]^{1/2}} \qquad \text{--- (3.68)}$$

where α_c is a dimensionless parameter corresponding to the streamlines $\psi_{(r,\theta)} = C$

Now for the purpose of numerical computation of the above integral, a normalised dimensionless time of half circulation is defined by

$$t'_{c\frac{1}{2}} = \oint \frac{\left[(dx)^2 + (x\,d\theta)^2\right]^{1/2}}{\left[v'^{\,2}_{r(x,\theta)} + v'^{\,2}_{\theta(x,\theta)}\right]^{1/2}} \qquad \text{--- (3.69)}$$

In terms of $t'_{c\frac{1}{2}}$, the actual time of half circulation $t_{c\frac{1}{2}}$ can be expressed as

$$t_{c\frac{1}{2}} = \frac{d}{V_o} \cdot \frac{1}{9} \cdot t'_{c\frac{1}{2}} \qquad \text{--- (3.70)}$$

The weighted average of the half time of circulation $\bar{t}_{c\frac{1}{2}}$ is thus given by

$$\bar{t}_{c\,1/2} = \frac{1}{9} \cdot \frac{d}{V_0} \quad \bar{t}'_{c\,1/2} \qquad \text{--- (3·71)}$$

where

$$\bar{t}'_{c\,1/2} = \frac{\int_0^{2\cdot73} t'_{c\,1/2}(x)\, 2\pi x \; dx}{\int_0^{2\cdot73} 2\pi \; x \; dx} = \frac{2}{2\cdot73^2} \int_0^{2\cdot73} t'_{c\,1/2}\,(x)\; x \; dx \qquad \text{--- (3·72)}$$

thus the weighted average of the total time of circulation $\bar{t}_c$ is given by

$$\bar{t}_c = 2\,\bar{t}_{c\,1/2} = \frac{2}{9}\,\frac{d}{V_0}\,\bar{t}'_{c\,1/2} \equiv \frac{d}{V_0}\,\bar{\alpha}_c \qquad \text{--- (3·73)}$$

where

$$\alpha_c = \frac{0\cdot536}{9} \int_0^{2\cdot73} t'_{c\,1/2}\;(x)\; x \; dx = \frac{\bar{t}_c}{9} \qquad \text{--- (3·74)}$$

Numerical evaluation of integral (3.69) and (3.72) yields

$$\bar{t}_c = 17\cdot8$$

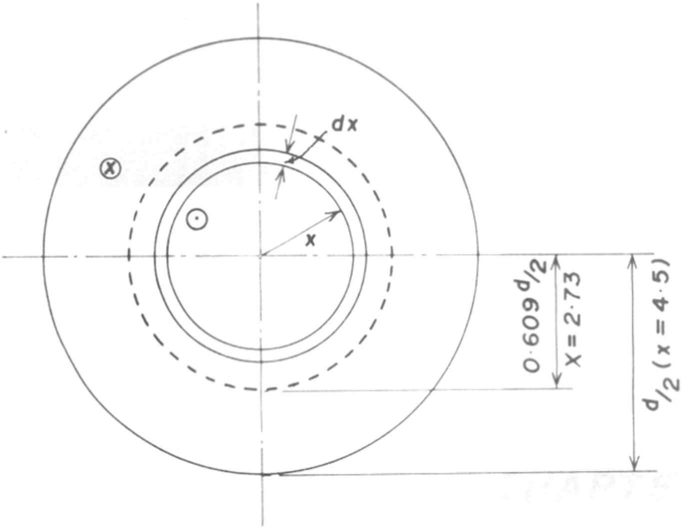
thus

$$\bar{\alpha}_c = \frac{17\cdot8}{9} \approx 2 \qquad ---(3\cdot75)$$

and

$$\bar{t}_c = 2\,\frac{d}{V_o} \qquad ---(3\cdot76)$$

α_c is a dimensionless quantity and in the present case serves as a correlation parameter between experimental and theoretical observations. The integrations involved, however, cannot be performed explicitly, and as such they were performed on an IBM 7044 computer.



(FIG. 3·2)

SCHEMATIC DIAGRAM FOR WEIGHTED AVERAGING

CHAPTER - 4

ESTIMATION OF MASS TRANSFER COEFFICIENT FOR FORMING DROP

CHAPTER - 4

ESTIMATION OF MASS TRANSFER COEFFICIENT FOR FORMING DROP

In this section an expression is derived for the mass transfer coefficient in the presence of internal circulation making use of the modified treatment of Handlos and Baron (32) which is presumably free from any parameter that must be determined empirically from experiments. The mechanism proposed by them is essentially based on the eddy diffusion model in which a droplet of constant diameter d of known dispersed phase viscosity, μ_D, is seen to fall with a known velocity, V, through a continuous phase of viscosity, μ_C, while the continuous phase resistance to diffusion is assumed to be vanishingly small. Further, a fully developed circulation pattern is assumed to be developed which is approximated by a system of coaxial tori rotating en-bloc with an average time of circulation (Fig. 4.1). It is further assumed that there is a random radial vibration superimposed upon the laminar flow causing, thereby, an admixing of adjacent streamlines. This eddy diffusion mechanism is presumed to be responsible for the radial mass transfer. At this stage, they assumed an effective eddy diffusivity, $\bar{E}'$, given by the Einstein equation for the two dimensional flow

$$\bar{E}' = \frac{\bar{Z}^2}{4\bar{t}_c} \qquad --- (4\cdot1)$$

where $\bar{Z}^2$ is the mean squared radial displacement during the average time of circulation. The above is true in the limiting case of complete mixing of one element of fluid in the characteristic time of circulation, that is, time for one complete circulation.

The average time of circulation $\bar{t}_c$ was obtained by Kronig and Brink (33) for the Hadamard-Rybczinski (29, 31) streamline pattern by solving the corresponding Fourier-Poisson equation, the relation being

$$\bar{t}_c = \frac{16}{3}\cdot\frac{d}{V}\left(1 + \frac{\mu_D}{\mu_C}\right) \qquad --- (4\cdot2)$$

Solution of the two-dimensional diffusion equation with $\bar{E}'$ as the effective diffusion coefficient having radial dependence, subject to appropriate boundary conditions, yielded in their case an effective mass transfer coefficient

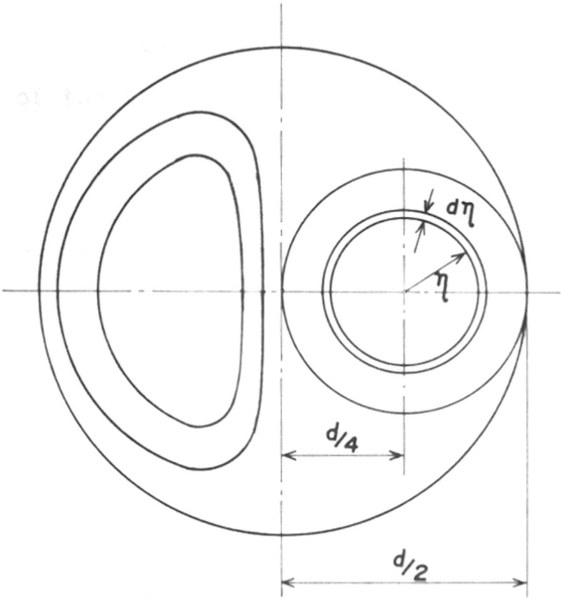
$$k_i = \frac{0\cdot00375\,V}{\left(1 + \frac{\mu_D}{\mu_C}\right)} \qquad --- (4\cdot3)$$

It is easily appreciated that the above model does not answer the problems imposed by the forming drop in that the drop diameter is varying continuously.

The internal circulation is not due to the viscous drag and as such the Hadamard-Rybczinski streamline cannot be used for calculating the average time of circulation as done by Kronig and Brink.

One can, however, solve this problem by the method of stepwise adiabatic solution referred to earlier. Accordingly it can be assumed that the streamline pattern of internal circulation as deduced in Chapter 3 will hold for any instantaneous drop diameter, and the average time of circulation for the streamline can be computed. This average time is then substituted in the eddy diffusion equation in place of the average time as computed by Kronig and Brink (33).

The diffusion equation governing the mass transfer is then solved, using the above eddy diffusion coefficient, for the proper boundary conditions (i.e. changing drop diameter). Thus the effect of mass injection is taken into account only to the extent that it provides the internal circulation, and changes the surface area available for mass transfer. The rest of the treatment proceeds along a line similar to that of Handlos and Baron (32). The mathematical treatment is as follows :



(FIG. 4·1)

A schematic drawing of a droplet having an instantaneous diameter d is shown in Fig. (4.1), in which the streamline pattern of the TE_{101} mode is replaced, as shown in the left half of the figure, by a system of tori with a maximum cross sectional radius of $d/4$ shown on the right half of the figure. On the assumption of a random radial motion, the mean squared displacement $\overline{Z^2}$ of the descriptive element initially at the radial distance, η, in course of one complete circulation period, can be easily deduced from the following phase - space arguments. The differential probability, $P(\eta)d\eta$, of the elemental volume initially at radial distance, η, to be found in an annulus, $\eta' \pm \frac{1}{2} \Delta \eta'$, after one complete circulation time, is equal to the fractional volume of the annulus. That is

$$P(\eta')\, d\eta' = \frac{2\pi\eta'\, d\eta'}{\pi d^2/16}$$

$$P(\eta')\, d\eta' = \frac{32\,\eta'\, d\eta'}{d^2} \qquad \text{--- (4.4)}$$

where d is the instantaneous drop diameter or

$$P(y')\, dy' = 2y'\, dy' \qquad \text{--- (4.5)}$$

$$y = \frac{4\eta}{d} \qquad \text{--- (4.6)}$$

y is a dimensionless variable whose value is given by

$$0 \leq y \leq 1$$

$$0 \leq \eta \leq \frac{d}{4}$$

The mean squared displacement is

$$\bar{Z}^2 = \int_0^1 Z^2(y')\, P(y')\, dy' \qquad \text{--- (4.7)}$$

with

$$Z^2(y) = \frac{d^2}{16}\,(y'-y)^2 \qquad --- \quad (4\cdot 8)$$

on integration, one obtains,

$$\bar{Z}^2\,(y) = \frac{d^2}{96}\,(6y^2 - 8y + 3) \qquad --- \quad (4\cdot 9)$$

The characteristic time for average displacement (which is the same as the average circulation time) is given from the previous calculation [Equation (3.75)]

$$\bar{t}_c = 2\,\frac{d}{V_o}$$

Thus, the effective diffusivity, $\bar{E}'(y)$, is given by

$$\bar{E}'(y) = \frac{\bar{Z}^2}{4\bar{t}_c} = \frac{d^2}{96}\cdot\frac{V_o}{8d}\,(6y^2 - 8y + 3)$$

$$\bar{E}'(y) = \frac{dV_o}{768}\,(6y^2 - 8y + 3) \qquad --- \quad (4\cdot 10)$$

The differential mass balance on the system within the torus is described by the diffusion equation in two dimension.

$$\frac{\partial c(\eta)}{\partial t} = div \left[\bar{E}' (y) \, grad \, c \, (\eta) \right] \quad --- (4\cdot11)$$

Where the argument, η, was retained in $c(\eta)$ to emphasise the exclusive radial dependence of concentration. In the polar co-ordinates, preferred because of the symmetry of the problem and the boundary conditions, the continuity equation can be rewritten as,

$$\frac{\partial c}{\partial t} = \frac{16}{d^2} \cdot \frac{1}{y} \cdot \frac{\partial}{\partial y} \left[\frac{V_0 \, yd}{768} (6y^2 - 8y + 3) \frac{\partial c}{\partial y} \right] \quad --- (4\cdot12)$$

$$\frac{\partial c}{\partial t} = \frac{16}{d} \cdot \frac{1}{y} \cdot \frac{\partial}{dy} \left[\frac{V_0 \, y}{768} (6y^2 - 8y + 3) \frac{\partial c}{\partial y} \right] \quad --- (4\cdot13)$$

where use is made of the fact that the derivatives on the right hand side are all at a given instant of time i.e. (t = const.). This justifies taking d outside the sign of differentiation with respect to y ($= 4\eta/d$) even though d is now a function of time. This amounts to treating t and y as independent variables. The obvious advantage of this choice of variables is the fact that the boundary of the growing toroid is given by y = 1 for all values of t.

In deducing Equation (4.13) we have made use of a relation from vector analysis (no phi variation)

$$\operatorname{div} \vec{A} \equiv \frac{1}{\eta} \left[\frac{\partial}{\partial \eta} (\eta A_\eta) + \frac{\partial}{\partial \theta} (A_\theta) \right] \qquad \text{--- } (4.14)$$

for any vector A in polar co-ordinates (η, θ). Equation (4.13) is to be solved for the boundary condition. Since it is assumed that the continuous phase resistance is negligible for the mass transfer taking place from the dispersed phase to the continuous phase, the concentration at the dispersed phase boundary is zero at any instant $t > 0$. Also, initially at time $t = 0$, the concentration at any point inside the drop will be equal to the initial (inlet) concentration c_o. Thus,

$$c = 0 \quad \text{at} \quad \eta = \frac{d}{4} \quad \text{or} \quad y = 1$$

$$\text{for} \quad t > 0$$

$$c = c_o \quad \text{at} \quad 0 \leq \eta \leq \frac{d}{4} \quad \text{or}$$

$$0 \leq y \leq 1$$

$$\text{for} \quad t = 0 \qquad \text{--- } (4.15)$$

The explicit time dependence of d is known from the volumetric rate of inflow, Q_v

$$Q_v = \frac{dv}{dt} = \frac{d}{dt}\left(\frac{\pi}{6} d^3\right) = \text{Const.} \qquad (4.16)$$

or

$$d = St^{1/3} \qquad --- (4.17)$$

where s is a constant given by

$$S = \left(\frac{6Q_v}{\pi}\right)^{1/3}$$

Equation (4.13) is separable and we can write

$$c_{(y,t)} = T_{(t)} \; Y_{(y)} \qquad --- (4.18)$$

$$\frac{\partial c_{(y,t)}}{\partial t} = Y_{(y)} \frac{\partial T_{(t)}}{\partial t} \qquad --- (4.19)$$

$$\frac{\partial c_{(y,t)}}{\partial y} = T_{(t)} \frac{\partial Y_{(y)}}{\partial y} \qquad --- (4.20)$$

Substituting Equations (4.17), (4.19) and (4.20) in Equation (4.13)

$$\frac{St^{1/3}}{T(t)} \cdot \frac{\partial T(t)}{\partial t} = \frac{1}{Y(y)} \cdot \frac{16}{y} \cdot \frac{\partial}{\partial y}\left[\frac{V_0 y}{768}(6y^2 - 8y + 3)\frac{\partial Y(y)}{\partial y}\right] \qquad --- (4.21)$$

After rearranging Equation (4.21) one can write

$$48\frac{S}{V_o}\cdot\frac{t^{1/3}}{T(t)}\cdot\frac{\partial T(t)}{\partial t}=\frac{1}{yY(y)}\cdot\frac{\partial}{\partial y}\left[y(6y^2-8y+3)\frac{\partial Y(y)}{\partial y}\right] \qquad ---(4\cdot 22)$$

$$48\frac{S}{V_o}\cdot\frac{t^{1/3}}{T(t)}\cdot\frac{\partial T(t)}{\partial (t)}=-\lambda \qquad ---(4\cdot 23)$$

$$\frac{1}{yY(y)}\cdot\frac{\partial}{\partial y}\left[y(6y^2-8y+3)\frac{\partial Y(y)}{\partial y}\right]=-\lambda \qquad ---(4\cdot 24)$$

where λ represents any one of an infinite number of eigen values.

Equation (4.23) can be easily integrated:

$$\int\frac{\partial T(t)}{T(t)}=-\frac{\lambda V_o}{48S}\int\frac{\partial t}{t^{1/3}}$$

$$\ln\ T(t)=-\frac{\lambda V_o}{48S}\cdot\frac{3}{2}t^{2/3}+\ln\ \text{const.} \qquad ---(4\cdot 25)$$

$$T(t)=\text{Const. exp.}\left[-\left(\frac{\lambda V_o}{32S}\cdot t^{2/3}\right)\right] \qquad ---(4\cdot 26)$$

Equation (4.24) is an eigen value equation exactly the same as the one solved by Handlos and Baron (32).

Let Y_n and λ_n be the n-th eigen function and eigen value respectively of Equation (4.24). The total solution can be written down as the linear combination of the eigen solution of Equation (4.24) multiplied by the appropriate time dependent function as obtained from (4.26) we have

$$c_{(y,t)} = c_o \sum_1^{\infty} \left[A_n Y_n \exp\left(\frac{\lambda_n V_o}{32S} t^{2/3} \right) \right] \qquad --- (4{\cdot}27)$$

where A_n is a constant to be evaluated from the boundary conditions. From the general properties of the eigen value problems each successive eigen value in Equation (4.27) is larger than the preceding one. Handlos and Baron have shown that the second eigen value is already large enough compared to the first to be neglected. Hence we retain only the lowest eigen value, this being

$$\lambda_1 = 2{\cdot}88$$

obtained by the Ragleigh-Ritz method.

Now the ratio of the mass of solute in the drop at time t to that at time zero is given by

$$\frac{M(t)}{M(o)} = 2 \sum_1^{\infty} A_n^2 \exp\left(- \frac{\lambda_n V_o}{32S} t^{2/3} \right) \qquad --- (4{\cdot}28)$$

Taking only the first eigen value in Equation (4.28) one obtains

$$\frac{M(t)}{M(o)} = 2 A_1^2 \exp\left(-\frac{\lambda_1 V_o}{32 S} t^{2/3}\right) \qquad --- (4\cdot 29)$$

We define the film coefficient by the following material balance equation

$$\frac{d}{dt}(v \; c_i) = k_i \; (c_{i,in} - c_i) \; A + \frac{dv}{dt} c_{io} \qquad --- (4\cdot 30)$$

where

v = instantaneous volume of the drops

A = instantaneous area of the drop

c_i = inside concentration at time t

$c_{i,in}$ = concentration at the interface

c_{io} = the inlet (initial) concentration c_i at $t = 0$

One gets from Equation (4.30) after differentiation

$$v \frac{dc_i}{dt} = k_i \; (c_{i,in} - c_i) \; A + \frac{dv}{dt}(c_{io} - c_i) \qquad --- (4\cdot 31)$$

As the inside concentration does not change appreciably during the formation time, the second term on the right hand side can be neglected, giving

$$v \frac{dc_i}{dt} = k_i \ (c_{i,in} - c_i) A \qquad ---(4.32)$$

where

$$\frac{v}{A} = \frac{d}{6} \quad \text{AND} \quad k_i \ c_{i,in} \approx 0$$

Equation (4.32) can be written as

$$\frac{d}{6} \cdot \frac{dc}{dt} = - k_i \, c \qquad ---(4.33)$$

In the above equation, substituting for d in Equation (4.17) and solving, one gets

$$\int_{c_o}^{c} \frac{dc}{c} = - \frac{6 k_i}{S} \int_{o}^{t} \frac{dt}{t^{1/3}} \qquad ---(4.34)$$

$$\ln c - \ln c_o = - \frac{9}{S} k_i \ t^{2/3} \qquad ---(4.35)$$

$$\frac{c}{c_o} = \exp\left(- \frac{9}{S} k_i \ t^{2/3} \right) \qquad ---(4.36)$$

$$\frac{c}{c_o} = \frac{M(t)}{M(o)}$$

Combining Equation (4.36) with Equation (4.29) one gets

$$\frac{9}{S}\ k_i\, t^{2/3} = \frac{\lambda_1 V_0}{32 \cdot S}\ t^{2/3} \qquad \text{---} \ (4\cdot37)$$

$$k_i = \frac{\lambda_1 V_0}{288} \qquad \text{---} \ (4\cdot38)$$

where $\lambda_1 = 2.88$. Thus

$$k_i = \frac{2\cdot88}{288}\, V_0 = 0\cdot01\, V_0 \qquad \text{---} \ (4\cdot39)$$

Equation (4.39) expresses the effective mass transfer coefficient in terms of fluid velocity V_o at the instantaneous centre of the drop. As discussed later in Chapter 6, V_o can reasonably be approximated by V_N, the nozzle velocity which is known. Thus

$$k_i = 0\cdot01\, V_0 \approx 0\cdot01\, V_N \qquad \text{---} \ (4\cdot40)$$

Equation (4.40) will be made use of in Chapter 6 for comparison of experimental mass transfer rates with the theoretical prediction.

CHAPTER–5

EXPERIMENTAL

CHAPTER - 5

EXPERIMENTAL

In Chapter 4 equations were developed based on the proposed conceptual model for estimating the average mass transfer coefficient during drop formation. From this equation it is possible to calculate k_i without experimental data. The purpose of the present chapter is to indicate a procedure for estimating k_i from experimental data, followed by a description of the experimental procedure and a tabulated presentation of the data obtained.

5.1 EVALUATION OF THE AVERAGE MASS TRANSFER COEFFICIENT k_i FOR A FORMING DROP FROM EXPERIMENTAL DATA

The experimental data were obtained in the form of an extraction efficiency E_T defined as

$$E_T = \frac{M_T}{M_\infty} \qquad --- (5 \cdot 1)$$

where M_T is the net mass transferred per drop at any time t and M_∞ is the theoretical maximum mass transfer than can take place after an infinite time of contact (i.e. mass transfer at equilibrium). Thus,

$$M_T = \int_0^{t_{max}} N'' \, dt \qquad --- (5 \cdot 2)$$

where N'' is the drop flux expressed as (gm-mole/sec. per drop). The average mass transfer coefficient for a forming drop is given by the equation

$$M_T = k_i \, \triangle c \; A_{AV} \, t \qquad --- (5 \cdot 3)$$

Expressing the average area $A_{av.}$ in terms of an appropriate integral the following equation results,

$$M_T = k_i \, \triangle c \int_0^{t_{max}} A \, dt \qquad --- (5 \cdot 4)$$

In this equation if the integral can be evaluated, then all other factors being known, k_1 can be estimated. The procedure for evaluating the integral is given below.

In the experimental programme organised for determining k_1, the volumetric flow rate of the liquid through the nozzle was held constant for a given run, i.e.

$$\frac{dv}{dt} = Const. = V_N \quad A_N \qquad \text{---(5.5)}$$

By writing the volume in terms of the radius and rearranging, the following equation results :

$$dt = \frac{4\pi}{V_N A_N} \cdot r^2 dr \qquad \text{---(5.6)}$$

Substituting Equation (5.6) in Equation (5.4) and suitably altering the boundary conditions, we obtain

$$M_T = k_i \; \triangle c \; \frac{(4\pi)^2}{V_N A_N} \int_0^{t_f} r^4 \, dr \qquad \text{---(5.7)}$$

$$M_T = k_i \, \triangle c \, \frac{(4\pi)^2}{V_N A_N} \cdot \frac{r_f^5}{5} \qquad \text{---(5.8)}$$

which can be written in terms of gm. transferred per cm.^{3} as

$$M_T = k_i \; \triangle c \; \frac{(4\pi)^2}{V_N A_N} \cdot \frac{r_f^5}{5} \cdot \frac{M}{v} \quad 10^{-3} \qquad \text{---(5.9)}$$

The mass transfer at infinite time of contact, again expressed in terms of gm./cm.^{3}, is given by

$$M_\infty = c^* \; M \; 10^{-3} \qquad \text{--- (5·10 a)}$$

$$M_\infty = c_o \; M \; 10^{-3} \qquad \text{--- (5·10 b)}$$

Substituting Equation (5.9) and (5.10a) (5.10b) respectively in Equation (5.1) and expressing v in terms of the radius and simplifying, we obtain

$$E_T = \frac{12}{5} k_{i2} \frac{\pi}{A_N V_N} \cdot \frac{\Delta c}{c^*} r_f^2 \qquad \text{--- (5·11 a)}$$

$$E_T = \frac{12}{5} k_{i1} \frac{\pi}{A_N V_N} \frac{\Delta c}{c_o} r_f^2 \qquad \text{--- (5·11 b)}$$

which on further simplification gives

$$k_{i2} = 0{\cdot}1326 \; A_N V_N \frac{c^*}{\Delta c} \frac{E_T}{r_f^2} \qquad \text{--- (5·12 a)}$$

$$k_{i1} = 0{\cdot}1326 \; A_N V_N \frac{c_o}{\Delta c} \frac{E_T}{r_f^2} \qquad \text{--- (5·12 b)}$$

It will be noticed that k_i calculated from Equations (5.12a) and (5.12b) has the dimensions of cm./sec. which is in keeping with the definition of k_i.

In order to obtain k_i from Equations (5.12a) and (5.12b) the values of c_o , c^* and Δc should be known, A_N, V_N and r_f being parametric constants for a given system and flow rate. E_T can be experimentally determined. The calculation of Δc is based on the direction of transfer, i.e. whether the transfer takes place from the forming drop to the continuous phase or vice versa. The following equations for Δc can easily be developed for the two cases based on dispersed phase resistance :

Case 1. Mass transfer from drop to continuous phase :

$$\Delta c = \frac{2c_o - c_1}{2} \qquad ---(5\cdot 13)$$

Case 2. Mass transfer from continuous phase to drop :

$$\Delta c = \frac{2c^* - c_t}{2} \qquad ---(5\cdot 14)$$

Equations for directly calculating k_i from experimental data and the parametric constants of a system can then be obtained by combining Equations (5.12b) and (5.13) for Case 1 and Equations (5.12a) and (5.14) for Case 2. Thus,

$$\text{Case 1.} \quad k_{i1} = 0 \cdot 1326 \; A_N V_N \; \frac{2c_o}{2c_o - c_1} \cdot \frac{E_T}{r_f^2} \qquad --- (5 \cdot 15)$$

$$\text{Case 2.} \quad k_{i2} = 0 \cdot 1326 \; A_N V_N \; \frac{2c^*}{2c^* - c_t} \cdot \frac{E_T}{r_f^2} \qquad --- (5 \cdot 16)$$

5.2 DESCRIPTION AND OPERATION OF THE EXPERIMENTAL ASSEMBLY

This section is concerned with the description of the experimental set-up used for determining the mass transfer coefficients during drop formation, and with the operation of this assembly. The purity of the chemicals used and the analytical technique employed are also discussed.

5.2.1 Description

The experimental set-up used in this study was of the conventional type and had the following broad features (Fig. 5·1): arrangements for constant feed of the continuous and dispersed phases; nozzle for drop formation; and an arrangement for withdrawing the drops immediately after formation.

The extraction was carried out in a glass column 75 mm. i. dia. x 550 mm. height. This was a double-walled column (1) in which the annular space (2) was used for circulating a thermostatic liquid for maintaining the temperature inside the column at any desired value. The bottom of the column was provided with an inlet for the dispersed phase, and to this inlet was attached a nozzle (3) machined from stainless steel. The internal diameter of the nozzle used was 1.9 mm. with a 45° taper; It was machined to ensure a sharp and well defined edge.

The column was fed at the top with the continuous phase which was continuously withdrawn at the bottom and collected in a vessel (5) through a jack leg. A constant flow rate of this phase was ensured through the use of a Mariotte bottle (4) and was measured with a differential manometer (6).

The dispersed phase was also fed from a Mariotte bottle (7) and it entered the nozzle through two double-surface heat exchangers (8) made of glass. The rate of the dispersed phase was accurately controlled by a fine needle valve (9), and the constancy of the rate was ensured through the differential manometer (10).

In order to maintain the entire system at a constant temperature (in this case 25°C.) water from thermostat (11) was circulated by an immersion pump both through the annular space of the extraction column and the two heat exchangers used in the dispersed phase line.

The object of the present experimental study being the measurement of mass transfer during drop formation, an inverted

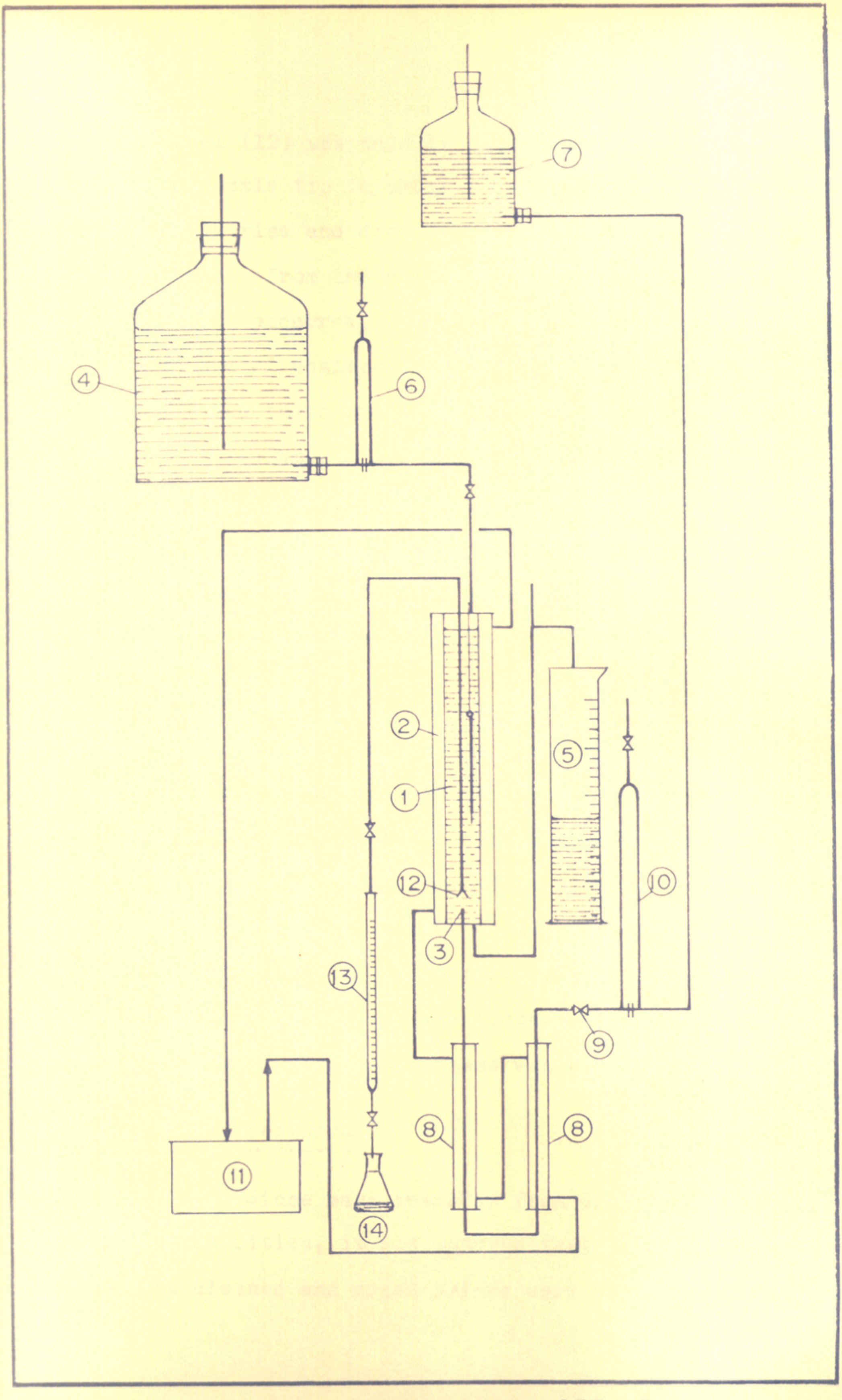


FIG. (5·1). EXPERIMENTAL SET-UP.

funnel (12) was held in position at a suitable distance from the nozzle tip in order to minimize the mass transfer during steady rise and drop coalescence. As soon as the drop was released from the nozzle tip, it entered the funnel where coalescence occurred, and it was therefore necessary to keep the surface of coalescence as small as possible in order to eliminate the third stage of mass transfer occurring in an experimental column. The second stage could be effectively minimized by maintaining as small a distance as possible between the funnel and nozzle tip. It was found that both these could be achieved by maintaining a distance of 12 mm. between the nozzle tip and funnel and by using a funnel with a coalescence surface of 32 sq. mm.

In order to ensure that the experiments were carried out under conditions where impurities from the set-up did not enter the system, the entire assembly was constructed of glass including the connecting lines except nozzle (3) and needle valve (9) which were made of stainless steel. Contamination from the connecting plastic rubber tubings was avoided by ensuring face to face contact between the glass tubings. The use of stop-cock grease was also avoided.

5.2.2 Operation

Since mass transfer from drops is extremely sensitive to impurities, it was ensured that the experimental assembly was cleaned and dried before work was commenced. This was accomplished by washing the entire equipment successively with tap water, detergent, tap water, dilute sulphuric acid, tap water, and double distilled water. It was then dried under vacuum. The continuous and the dispersed phases were mutually saturated and stored together for at least a month in a well-cleaned glass container before use.

The run was commenced by adjusting the flow of the continuous phase from the Mariotte bottle at a constant rate of 100 cc. per min. corresponding to the velocity of the continuous phase equal to 0.377 mm. per sec. The flow was such that there was no disturbance and the liquid was continuously removed from the bottom through the jack let as described earlier. The rate of the continuous phase flow was measured by collecting a known volume of the liquid. Although the differential manometer was accurately calibrated before the commencement of the runs, the actual rate was also determined by measuring the time required for collecting a known volume in order to provide a double check on the flow rate.

The dispersed phase flow was also started so that drops were continuously released from the nozzle into the inverted funnel. Periodic counting of the drops ensured that the rate of drop formation was constant. As in the case of the continuous phase, this was checked by collecting and measuring 100 drops in a receiver and comparing the flow rate obtained with the rates read from the number of drops per unit time and the differential manometer reading.

The circulation of water from the thermostat was now commenced so that the entire system was maintained at a temperature of 25.0 ± 0.20°C. Steady conditions were reached after about 2-3 hours depending on the flow rates.

After steady conditions had been obtained the liquid was collected in the microburette, and 10 cc. of this was diluted with 100 cc. of distilled water and titrated against standard KOH using a Beckman automatic titrator (type-K). The automatic titrator was provided with standard glass electrode, a reference electrode and an efficient high speed stirrer. The delivery tip of the microburette was immersed in the liquid very close to the stirrer. The analytical technique was accurate to within ± 0.1%.

Materials used :

Two solvents were used as the dispersed phase (drop phase), benzene and toluene. Rectified grade toluene was purified three times with conc. H_2SO_4 to remove any traces of thiophene. It was then washed repeatedly with water, once with 10% NA_2CO_3 solution, and again with water. It was distilled in an all-glass 24 inch distillation column packed with 1/8" glass helices (equivalent to 20 theoretical plates). The first 100 cc. of the product and the last 100 cc. were discarded. The fraction in the boiling point range 107 - 108°C. was collected.

Benzene of BDH rectified grade was purified in the same way as mentioned above and the boiling point range of 78.5 - 79.5°C. was collected.

The water used for the continuous phase (and for other purposes during the experiments) was of glass distilled grade.

Analar grade solutes (acetic acid and propionic acid) were used.

5.3 EXPERIMENTAL DATA

Experimental data were collected for the following four systems :

Acetic acid - toluene - water
Acetic acid - benzene - water
Propionic acid - toluene - water
Propionic acid - benzene - water

By carrying out experiments for both the directions of transfer for a given system, it was possible to organize 8 series of experiments. The results obtained are summarized in Tables (5.1) through (5.8), which also include the values of the constant, β, and the theoretical mass transfer coefficient, k_i. A comparison of the experimental and theoretical values is made in Chapter 6. A sample calculation of k_i is given below.

Calculation of k_i

The procedure for computing the mass transfer coefficient, k_i, from the experimental data is demonstrated for run No.080 of Table (5.5) for the system propionic acid - toluene - - water, the direction of transfer being from the continuous to the dispersed phase, using Equation (5.16).

$$k_{i2}(\text{exp.}) = 0.1326\ A_N V_N \left(\frac{2\ c^*}{2c^* - \ c_t} \right) \frac{E_T}{{r_f}^2}$$

where

A_N = 0.02835 cm.^{2}

V_N = 1.145 cm./sec.

c^* = 0.346 gm.mole/litre

c_t = 0.04960 gm.mole/litre

E_T = 0.1433

r_f = 0.260 cm.

Substituting **these** values in the above equation

$$k_{i2}(\text{exp.}) = 0.1326 \times 0.02835 \times 1.145 \ \frac{2\text{x}0.346}{2\text{x}0.346-0.04960} \cdot \frac{0.1433}{0.0678}$$

$$= 0.0098 \text{ cm./sec.}$$

$k_i(\text{theoretical}) \ = \ 0.01\ V_N$

$k_{i2}(\text{exp.}) \ = \ \beta\ V_N$ --- (5·17)

il

where β is the experimental constant whose theoretical value is 0.01

$$\beta = 0.01 \frac{k_{12}(\text{exp.})}{k_1(\text{theor})} = 0.01 \frac{0.0098}{0.01145}$$

$$\beta = 0.00855$$

TABLE (5.1)

EXPERIMENTAL DATA FOR THE SYSTEM : ACETIC ACID - TOLUENE - WATER

Direction of transfer : from continuous to dispersed phase

Temperature : 25°C.

I. D. of nozzle : 0.19 cm.

S.No.	t_f sec.	r_f cm.	$c^* \times 10^2$ $\frac{\text{gm.mole}}{\text{lit.}}$	$c_t \times 10^3$ $\frac{\text{gm.mole}}{\text{lit.}}$	$E_T \times 10$	V_N $\frac{\text{cm.}}{\text{sec.}}$	k_i(exp.) $\frac{\text{cm.}}{\text{sec.}}$	k_i(theo.) $\frac{\text{cm.}}{\text{sec.}}$	β
1	2	3	4	5	6	7	8	9	10
000	3.25	0.272	3.33	5.12	1.536	0.912	0.00771	0.00912	0.00845
001	2.25	0.272	3.33	4.16	1.250	1.333	0.00903	0.01333	0.00676
002	1.60	0.273	3.33	3.94	1.171	1.896	0.01189	0.01896	0.00626
003	4.10	0.272	3.33	4.86	1.460	0.723	0.00578	0.00723	0.00798
004	5.10	0.271	3.33	5.61	1.683	0.575	0.00540	0.00575	0.00941
005	6.15	0.271	3.33	5.94	1.785	0.477	0.00478	0.00477	0.01003
006	7.18	0.271	3.33	6.23	1.875	0.408	0.00432	0.00408	0.01058
011	1.80	0.273	3.33	4.31	1.295	1.685	0.01176	0.01685	0.00697
012	2.60	0.273	3.33	4.46	1.340	1.167	0.00844	0.01167	0.00723

1	2	3	4	5	6	7	8	9	10
013	1.50	0.273	3.33	4.53	1.360	2.022	0.01487	0.02022	0.00735
014	1.35	0.273	3.33	4.46	1.340	2.247	0.01626	0.02247	0.00723
015	1.20	0.273	3.33	4.53	1.360	2.528	0.01859	0.02528	0.00735
016	0.63	0.273	3.33	4.61	1.384	4.816	0.03608	0.04816	0.00685
017	0.73	0.273	3.33	3.86	1.160	4.156	0.02579	0.04156	0.00620
018	1.05	0.281	3.33	4.01	1.205	3.124	0.01906	0.03124	0.00610
019	0.96	0.281	3.33	3.64	1.095	3.417	0.01883	0.03417	0.00552
020	0.74	0.281	3.33	3.94	1.184	4.434	0.02655	0.04434	0.00598
021	0.68	0.281	3.33	4.01	1.205	4.824	0.02943	0.04824	0.00610
022	0.55	0.281	3.33	4.26	1.250	5.964	0.03790	0.05964	0.00635
023	1.70	0.280	3.33	4.60	1.380	1.909	0.01359	0.01909	0.00711
024	2.10	0.278	3.33	4.53	1.360	1.512	0.01073	0.01512	0.00709
025	2.10	0.278	3.33	4.68	1.405	1.512	0.01111	0.01512	0.00735
026	2.60	0.273	3.33	4.90	1.470	1.167	0.00933	0.01167	0.00799
027	3.00	0.273	3.33	5.05	1.516	1.011	0.00836	0.01011	0.00826
028	3.25	0.273	3.33	5.20	1.560	0.933	0.00796	0.00933	0.00852
029	3.48	0.273	3.33	5.27	1.584	0.872	0.00756	0.00872	0.00866
030	4.70	0.272	3.33	5.35	1.605	0.630	0.00559	0.00630	0.00886

1	2	3	4	5	6	7	8	9	10
031	4.86	0.272	3.33	5.20	1.560	0.610	0.00524	0.00610	0.00859
032	5.60	0.272	3.33	5.57	1.673	0.529	0.00491	0.00529	0.00927
033	6.90	0.272	3.33	6.16	1.850	0.429	0.00445	0.00429	0.01033
034	3.90	0.272	3.33	5.27	1.584	0.760	0.00664	0.00760	0.00873
044	3.66	0.253	7.56	12.10	1.600	0.655	0.00669	0.00655	0.01020
045	3.70	0.253	7.56	11.87	1.570	0.648	0.00649	0.00648	0.01000
046	3.00	0.253	7.56	11.58	1.531	0.780	0.00779	0.00780	0.00973
047	3.00	0.253	7.56	11.65	1.542	0.780	0.00785	0.00780	0.00980
048	2.40	0.253	7.56	10.97	1.453	1.000	0.00920	0.01000	0.00918
049	2.00	0.255	7.56	10.67	1.413	1.235	0.01080	0.01235	0.00875
050	2.58	0.255	7.56	10.60	1.403	0.957	0.00831	0.00957	0.00868
051	1.26	0.258	7.56	10.10	1.335	2.016	0.01628	0.02016	0.00806
052	2.02	0.260	7.56	9.50	1.257	1.292	0.00975	0.01292	0.00753
053	0.94	0.260	7.56	9.06	1.198	2.777	0.01962	0.02777	0.00706
054	0.78	0.260	7.56	9.13	1.207	3.346	0.02383	0.03346	0.00711
055	0.70	0.260	7.56	9.13	1.207	3.729	0.02656	0.03729	0.00711
056	0.57	0.260	7.56	9.50	1.257	4.579	0.03406	0.04579	0.00742
057	0.52	0.260	7.56	8.68	1.148	5.020	0.03390	0.05020	0.00675

1	2	3	4	5	6	7	8	9	10
058	0.50	0.260	7.56	8.17	1.070	5.220	0.03274	0.05220	0.00627
059	5.40	0.251	7.56	15.20	2.012	0.431	0.00575	0.00431	0.01335
060	4.30	0.251	7.56	15.20	2.012	0.541	0.00723	0.00541	0.01335
061	0·58	0.260	7.56	8.74	1.168	4.500	0.03093	0.04500	0.00686

TABLE (5.2)

EXPERIMENTAL DATA FOR THE SYSTEM : ACETIC ACID - TOLUENE - WATER

Direction of transfer : from dispersed to continuous phase

Temperature : 25°C.

I. D. of nozzle : 0.19 cm.

S.No.	t_f sec.	r_f cm.	$c_o \times 10^2$ $\frac{\text{gm.mole}}{\text{lit.}}$	$c_1 \times 10^3$ $\frac{\text{gm.mole}}{\text{lit.}}$	$E_T \times 10$	V_N $\frac{\text{cm.}}{\text{sec.}}$	k_1(exp.) $\frac{\text{cm.}}{\text{sec.}}$	k_1(theo.) $\frac{\text{cm.}}{\text{sec.}}$	β
1	2	3	4	5	6	7	8	9	10
150	5.52	0.316	4.215	6.23	1.480	0.843	0.00507	0.00843	0.00600
151	5.52	0.316	4.215	6.03	1.430	0.843	0.00488	0.00843	0.00579
152	4.28	0.316	4.215	5.92	1.380	1.088	0.00607	0.01088	0.00557
153	4.28	0.316	4.215	5.92	1.380	1.088	0.00607	0.01088	0.00557
154	3.25	0.316	4.215	5.40	1.280	1.433	0.00737	0.01433	0.00513
155	3.25	0.316	4.215	5.65	1.340	1.433	0.00774	0.01433	0.00540
156	2.35	0.316	4.215	4.97	1.180	1.981	0.00934	0.01981	0.00471
157	2.35	0.316	4.215	5.06	1.200	1.981	0.00951	0.01981	0.00480

TABLE (5.3)

EXPERIMENTAL DATA FOR THE SYSTEM : ACETIC ACID - BENZENE - WATER

Direction of transfer : from continuous to dispersed phase

Temperature : 25°C.

I. D. of nozzle : 0.19 cm.

S.No.	t_f sec.	r_f cm.	$c^* \times 10^2$ $\frac{\text{gm.mole}}{\text{lit.}}$	$c_t \times 10^3$ $\frac{\text{gm.mole}}{\text{lit.}}$	$E_T \times 10$	V_N $\frac{\text{cm.}}{\text{sec.}}$	k_i (exp.) $\frac{\text{cm.}}{\text{sec.}}$	k_i (theo.) $\frac{\text{cm.}}{\text{sec.}}$	β
1	2	3	4	5	6	7	8	9	10
090	5.22	0.281	1.74	3.04	1.747	0.662	0.00603	0.00662	0.00910
091	3.62	0.289	1.74	2.67	1.535	0.984	0.00737	0.00984	0.00741
092	1.80	0.294	1.74	2.52	1.450	2.077	0.01411	0.02071	0.00680
093	1.90	0.294	1.74	2.45	1.410	1.968	0.01297	0.01968	0.00660
094	1.17	0.294	1.74	2.37	1.365	3.196	0.02034	0.03196	0.00636
096	6.62	0.276	3.15	5.64	1.790	0.469	0.00454	0.00469	0.00970
097	6.75	0.276	3.15	6.02	1.910	0.460	0.00478	0.00460	0.00942
098	4.75	0.276	3.15	5.50	1.745	0.653	0.00616	0.00653	0.00942
099	3.38	0.276	3.15	5.27	1.673	0.918	0.00826	0.00918	0.00900

1	2	3	4	5	6	7	8	9	10
100	2.85	0.276	3.15	5.27	1.672	1.089	0.00979	0.01089	0.00900
101	2.80	0.276	3.15	4.75	1.508	1.109	0.00891	0.01109	0.00804
102	2.34	0.278	3.15	4.82	1.530	1.357	0.01093	0.01357	0.00805
103	2.34	0.278	3.15	4.60	1.460	1.357	0.01039	0.01357	0.00766
104	1.72	0.278	3.15	4.31	1.367	1.846	0.01317	0.01846	0.00715
105	1.21	0.282	3.15	4.38	1.390	1.500	0.01060	0.01500	0.00707
106	1.25	0.282	3.15	4.38	1.390	2.653	0.01874	0.02653	0.00707
107	0.92	0.282	3.15	3.75	1.190	3.604	0.02156	0.03604	0.00598
108	0.72	0.282	3.15	3.64	1.154	4.605	0.02667	0.04605	0.00579
109	0.61	0.282	3.15	3.64	1.154	5.436	0.03148	0.05436	0.00579
111	2.26	0.272	5.95	8.70	1.495	1.311	0.01074	0.01311	0.00819
115	1.92	0.272	5.95	8.54	1.435	1.543	0.01212	0.01543	0.00786
116	2.44	0.267	5.95	8.35	1.403	1.157	0.00907	0.01157	0.00785
117	2.40	0.267	5.95	8.70	1.462	1.176	0.00964	0.01176	0.00820
118	1.65	0.267	5.95	7.80	1.310	1.710	0.01247	0.01710	0.00729
119	1.70	0.267	5.95	8.00	1.345	1.660	0.01244	0.01660	0.00750
120	5.68	0.272	6.77	12.80	1.892	0.509	0.00541	0.00509	0.01060
122	2.77	0.263	6.77	11.40	1.685	0.968	0.00966	0.00968	0.01000

TABLE (5.4)

EXPERIMENTAL DATA FOR THE SYSTEM : ACETIC ACID - BENZENE - WATER

Direction of transfer : from dispersed to continuous phase

Temperature : 25°C.

I. D. of nozzle : 0.19 cm.

S.No.	t_f sec.	r_f cm.	$c_o \times 10^2$ $\frac{\text{gm.mole}}{\text{lit.}}$	$c_1 \times 10^3$ $\frac{\text{gm.mole}}{\text{lit.}}$	$E_T \times 10$	V_N $\frac{\text{cm.}}{\text{sec.}}$	k_1(exp.) $\frac{\text{cm.}}{\text{sec.}}$	k_1(theo.) $\frac{\text{cm.}}{\text{sec.}}$	β
1	2	3	4	5	6	7	8	9	10
136	2.75	0.331	3.40	3.77	1.110	1.950	0.00787	0.01950	0.00403
137	2.80	0.331	3.40	4.08	1.203	1.915	0.00841	0.01915	0.00440
138	3.90	0.325	3.40	5.13	1.510	1.302	0.00756	0.01302	0.00580
139	3.90	0.325	3.40	4.18	1.230	1.302	0.00607	0.01302	0.00466
140	7.50	0.322	3.40	5.54	1.630	0.658	0.00424	0.00658	0.00643
141	7.85	0.322	3.40	5.63	1.660	0.629	0.00413	0.00629	0.00662

TABLE (5.5)

EXPERIMENTAL DATA FOR THE SYSTEM : PROPIONIC ACID - TOLUENE - WATER

Direction of transfer : from continuous to dispersed phase

Temperature : 25°C.

I. D. of nozzle : 0.19 cm.

S.No.	t_f sec.	r_f cm.	$c^* \times 10^2$ $\frac{\text{gm.mole}}{\text{lit.}}$	$c_t \times 10^3$ $\frac{\text{gm.mole}}{\text{lit.}}$	$E_T \times 10$	V_N $\frac{\text{cm.}}{\text{sec.}}$	k_i(exp.) $\frac{\text{cm.}}{\text{sec.}}$	k_i(theo.) $\frac{\text{cm.}}{\text{sec.}}$	β
1	2	3	4	5	6	7	8	9	10
062	1.35	0.274	17.2	21.20	1.233	2.247	0.01488	0.02247	0.00661
063	1.20	0.274	17.2	20.40	1.186	1.379	0.00876	0.01379	0.00636
064	2.98	0.276	17.2	23.76	1.380	1.042	0.00762	0.01042	0.00731
065	2.54	0.276	17.2	24.40	1.420	1.222	0.00921	0.01222	0.00750
066	0.90	0.274	17.2	19.60	1.140	3.370	0.02053	0.03370	0.00607
067	0.78	0.274	17.2	19.65	1.143	3.889	0.02376	0.03889	0.00611
068	3.20	0.272	17.2	25.80	1.500	0.904	0.00745	0.00904	0.00824
069	2.80	0.272	17.2	24.85	1.445	1.034	0.00817	0.01034	0.00790
070	2.40	0.272	17.2	23.80	1.385	1.205	0.00911	0.01205	0.00755

1	2	3	4	5	6	7	8	9	10
071	2.22	0.272	17.2	23.70	1.380	1.303	0.00981	0.01303	0.00752
072	2.18	0.272	17.2	23.90	1.390	1.327	0.01007	0.01327	0.00758
073	2.18	0.272	17.2	23.20	1.345	1.327	0.00972	0.01327	0.00732
074	1.50	0.273	17.2	21.40	1.240	1.975	0.01327	0.01975	0.00671
075	0.82	0.274	17.2	19.15	1.113	3.699	0.02197	0.03699	0.00593
078	2.22	0.260	34.6	50.00	1.445	1.176	0.01015	0.01176	0.00863
079	1.82	0.260	34.6	48.00	1.388	1.434	0.01186	0.01434	0.00826
080	2.28	0.260	34.6	49.60	1.433	1.145	0.09800	0.01145	0.00865
081	1.80	0.260	34.6	43.80	1.268	1.450	0.01088	0.01450	0.00760
082	1.00	0.260	34.6	39.00	1.127	2.610	0.01728	0.02610	0.00662
083	1.12	0.260	34.6	36.90	1.065	2.331	0.01454	0.02331	0.00623
084	1.05	0.260	34.6	37.00	1.070	2.486	0.01558	0.02486	0.00626
085	4.20	0.260	34.6	57.80	1.670	0.621	0.00628	0.00621	0.01010
086	0.81	0.260	34.6	36.00	1.042	3.223	0.01964	0.03223	0.00603
087	0.75	0.260	34.6	38.00	1.100	3.480	0.02246	0.03480	0.00645
088	0.53	0.260	34.6	34.90	1.007	4.925	0.02896	0.04925	0.00587
089	0.48	0.260	34.6	32.10	0.928	5.438	0.02934	0.05438	0.00539

TABLE (5.6)

EXPERIMENTAL DATA FOR THE SYSTEM : PROPIONIC ACID - TOLUENE - WATER

Direction of transfer : from dispersed to continuous phase

Temperature : 25°C

I. D. of nozzle : 0.19 cm.

S.No.	t_f sec.	r_f cm.	$c_o \times 10^2$ $\frac{\text{gm.mole}}{\text{lit.}}$	$c_1 \times 10^3$ $\frac{\text{gm.mole}}{\text{lit.}}$	$E_T \times 10$	V_N $\frac{\text{cm.}}{\text{sec.}}$	k_i(exp.) $\frac{\text{cm.}}{\text{sec.}}$	k_i(theo.) $\frac{\text{cm.}}{\text{sec.}}$	β
1	2	3	4	5	6	7	8	9	10
164	5.55	0.297	17.82	26.80	1.502	0.699	0.00484	0.00699	0.00691
165	5.52	0.297	17.82	28.32	1.589	0.703	0.00517	0.00703	0.00735
166	4.05	0.294	17.82	26.62	1.492	0.923	0.00647	0.00923	0.00699
167	4.01	0.294	17.82	26.45	1.483	0.932	0.00649	0.00932	0.00695
168	3.15	0.294	17.82	25.25	1.415	1.187	0.00786	0.01187	0.00661
169	2.90	0.294	17.82	24.57	1.380	1.289	0.00830	0.01289	0.00644
170	2.32	0.294	17.82	23.20	1.300	1.612	0.00974	0.01612	0.00603
171	2.05	0.294	17.82	22.87	1.282	1.824	0.01086	0.01824	0.00594
172	1.72	0.294	17.82	22.53	1.263	2.174	0.01274	0.02174	0.00586

1	2	3	4	5	6	7	8	9	10
173	1.12	0.294	17.82	21.00	1.178	3.338	0.01816	0.03338	0.00543
174	1.18	0.294	17.82	22.15	1.185	3.169	0.01735	0.03169	0.00547
175	0.93	0.294	17.82	19.80	1.110	4.020	0.02054	0.04020	0.00510
176	0.78	0.294	17.82	19.12	1.071	4.794	0.02358	0.04794	0.00491
177	0.71	0.294	17.82	19.46	1.090	5.266	0.02639	0.05266	0.00500
179	6.73	0.294	17.82	32.08	1.800	0.577	0.00486	0.00577	0.00842

TABLE (5.7)

EXPERIMENTAL DATA FOR THE SYSTEM : PROPIONIC ACID - BENZENE - WATER

Direction of transfer : from continuous to dispersed phase

Temperature : 25°C.

I. D. of nozzle : 0.19 cm.

S.No.	t_f sec.	r_f cm.	$c^* \times 10^2$ $\frac{\text{gm.mole}}{\text{lit.}}$	$c_t \times 10^3$ $\frac{\text{gm.mole}}{\text{lit.}}$	$E_T \times 10$	V_N $\frac{\text{cm.}}{\text{sec.}}$	k_i(exp.) $\frac{\text{cm.}}{\text{sec.}}$	k_i(theo.) $\frac{\text{cm.}}{\text{sec.}}$	β
1	2	3	4	5	6	7	8	9	10
126	1.30	0.301	1.85	2.30	1.275	3.093	0.01744	0.03093	0.00563
127	1.08	0.301	1.85	2.18	1.180	1.933	0.01004	0.01933	0.00519
128	3.62	0.301	1.85	2.50	1.356	1.111	0.00669	0.01111	0.00601
129	2.03	0.301	1.85	2.31	1.250	1.981	0.01093	0.01981	0.00552

TABLE (5.8)

EXPERIMENTAL DATA FOR THE SYSTEM : PROPIONIC ACID - BENZENE - WATER

Direction of transfer : from dispersed to continuous phase

Temperature : 25°C.

I. D. of nozzle : 0.19 cm.

S.No.	t_f sec.	r_f cm.	$c_o \times 10^2$ $\frac{\text{gm.mole}}{\text{lit.}}$	$c_1 \times 10^3$ $\frac{\text{gm.mole}}{\text{lit.}}$	$E_T \times 10$	V_N $\frac{\text{cm.}}{\text{sec.}}$	k_1(exp.) $\frac{\text{cm.}}{\text{sec.}}$	k_1(theo.) $\frac{\text{cm.}}{\text{sec.}}$	β
1	2	3	4	5	6	7	8	9	10
142	1.85	0.308	9.05	10.57	1.167	2.326	0.01141	0.02326	0.00490
143	1.13	0.308	9.05	9.18	1.131	3.808	0.01810	0.03808	0.00476
144	3.40	0.308	9.05	12.35	1.365	1.266	0.00734	0.01266	0.00580
145	2.31	0.308	9.05	11.38	1.255	1.863	0.00987	0.01863	0.00530
146	4.90	0.308	9.05	13.48	1.490	0.878	0.00559	0.00878	0.00636
147	3.40	0.308	9.05	12.03	1.329	1.266	0.00713	0.01266	0.00563
148	5.67	0.308	9.05	14.62	1.630	0.759	0.00533	0.00759	0.00701
149	6.10	0.308	9.05	13.97	1.542	0.705	0.00466	0.00705	0.00661

CHAPTER - 6

DISCUSSION

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DISCUSSION

6.1 KINEMATIC SIMILARITY

The theoretical model proposed in this study is predicated on the kinematic similarity between the streamlines of circulation in a forming drop and the field pattern in a spherical microwave cavity oscillating in TE_{101} mode. The kinematic analogy in turn is based on the similarity of the field equations governing the field variables in the two cases (velocity and the magnetic field respectively). While the kinematic similarity is by no means complete in that the dynamical features of the problem are not taken into account, nevertheless the significant points of similarity are covered in this phenomenological treatment.

For the completeness of any kinematic similarity, the boundary conditions must be reproduced in the model (Equations (3.11),(3.18)). This is indeed the case in the present treatment.

The circumstance of the changing boundary conditions (varying drop diameter) has been treated in the proposed model by making use of the mathematical orifice of stepwise adiabatic solution, which is justifiable in the present case as the time of one complete circulation in the drop is small compared to the total life of the forming drop. Thus the field equations contain the drop diameter as a time dependent parameter. It may be emphasised that the kinematic similarity envisaged here takes full cognizance of the fact that the field quantities inside the microwave cavity have a high frequency time dependence while the flow in the forming drop is relatively quasi-static. That we are still able to compare the instantaneous streamlines in the two cases derives from the fact that the streamline can be expressed in a parametric form involving space co-ordinates only. This resultant separability of space and time dependence of the field quantities forms the conceptual basis of the present treatment.

A significant point of departure from the earlier treatments based on the conventional Hadamard-Rybczinski model is in respect of the inclusion of the viscous effects. It may be noted that in the Hadamard model the internal circulation is exclusively the result of tangential viscous drag exerted by the continuous phase along the surface of the moving drop, and as such forms the core of the treatment. In particular, in the limit, the dispersed phase viscosity approaching zero, no internal circulation will be set up.

In the present model, which is apparently the only model proposed for a growing drop, viscous effects are of secondary importance. The internal circulation is exclusively due to the momentum impulse generated by the injection velocity. In point of fact, viscous forces have a deleterious effect on the internal circulation (which tends to reduce the value of V_o). The contrariness of the role of viscosity in the two models is noteworthy.

In the development of the model it is apparent that the important parameter is the velocity (V_o) at the instantaneous centre of the forming drop. Since V_o cannot be experimentally determined, it should be expressed in terms of the velocity at the nozzle (V_N) which is known. The exact determination of the ratio V_o/V_n appears to be well nigh impossible. It is, however, known from the solution of an analogous problem of an infinitesimally small submerged nozzle injecting a liquid vertically in an infinite medium (35) of the same liquid, that there is a finite depth of penetration in the direction of injection. It is reasonable to assume, for physical dimensions small compared to the penetration depth, that the velocity along the direction of injection is constant (i.e. equal to the injection velocity). In the present case, this amounts to assuming $V_o \approx V_n$ without significant loss of accuracy. Moreover the containment of the streamlines inherent in the present case tends to further equalise the velocities.

6.2 MASS TRANSFER

The theoretical model discussed in the foregoing section enables one to estimate the average time of circulation.

This has been done by previous investigators for the uniform moving drop on the basis of the Hadamard-Rybczinski model of internal circulation induced by the viscous drag. The subsequent use of this time of circulation in the estimation of the mass transfer coefficient has generally followed the treatment given by Handlos and Baron, in which one obtains an expression for the effective diffusivity from Einstein's equation. In the present work, while the average time of circulation has been calculated by an entirely new theoretical model, the basic tenets of the Handlos-Baron treatment have been retained in deriving the effective mass transfer coefficient.

The final expression for the mass transfer coefficient is strikingly similar to the one obtained by Handlos and Baron, in spite of the fact that in the present case the drop diameter is continually changing (since it involves a forming drop), while Handlos and Baron considered the case of a moving drop, the diameter of which is necessarily constant.

The viscosity dependent factor appearing in Handlos-Baron expression is inherent in the very mechanism responsible for the circulation, while in the present analysis it is a dissipative factor which is considered non-essential to the treatment.

It may be noted that the mass transfer coefficient derived is independent of the specific properties of the liquid. This is to be anticipated in view of the kinematic treatment employed in which the constitutive properties are not involved. An extension of this treatment to the non-ideal case must include the effects of viscosity, which can be accomplished phenomenologically by introducing a damping factor involving viscosity. However, this has not been attempted in the present treatment since, as shown in the next section, the idealised model adequately represents the experimental data.

6.3 TEST OF THE MODEL

The equation developed from the proposed conceptual model can be put in the general form

$$k_i = \beta V_n$$

The value of β has been theoretically estimated to be 0.01 in Chapter 4. Based on the experimental values of the mass transfer coefficient, including both the directions of transfer, presented in Tables (5.1) to (5.8) of Chapter 5, the values of β have been calculated for each of the 144 runs recorded in these tables. These values vary from about 0.005 to 0.01. The average value of β was then calculated by plotting k_i(exp.) vs. V_n and determining the slope by the method of least squares. Thus,

$$\beta = 0.00623$$

Standard deviation of the slope = 0.0001562

In order to provide a visual comparison of the experimental and theoretical mass transfer coefficients, a plot of k_i(theoretical) vs. k_i(exptl.) is presented in Fig. (6.1).

Considering the fact that the proposed model is a completely hypothetical one, involving kinematic similarity with an entirely different physical system, the correspondence between the theoretical (0.01) and experimental (0.00623) values of β should be regarded as highly satisfactory.

In Chapter - 2 all the existing models were brought to a common efficiency basis for comparison, and the values of the resulting equation

$$E = \alpha_2 \left(\frac{D t_f}{r_f^2} \right)^{1/2}$$

obtained from different models were summarized in Table (2.1). In order to compare the value of α_2 obtained from the present experimental programme with those reported this was estimated from the equation given above using the data presented in Tables (5.1) to (5.8) and by employing the method of least squares. Thus,

$$\alpha_2 = 5.142$$

Standard deviation = 0.0865

It will be seen from Table (2.1) that this value is only slightly lower than that calculated from the model of Heertjes et al. (17), but is higher than those predicted from the other models listed.

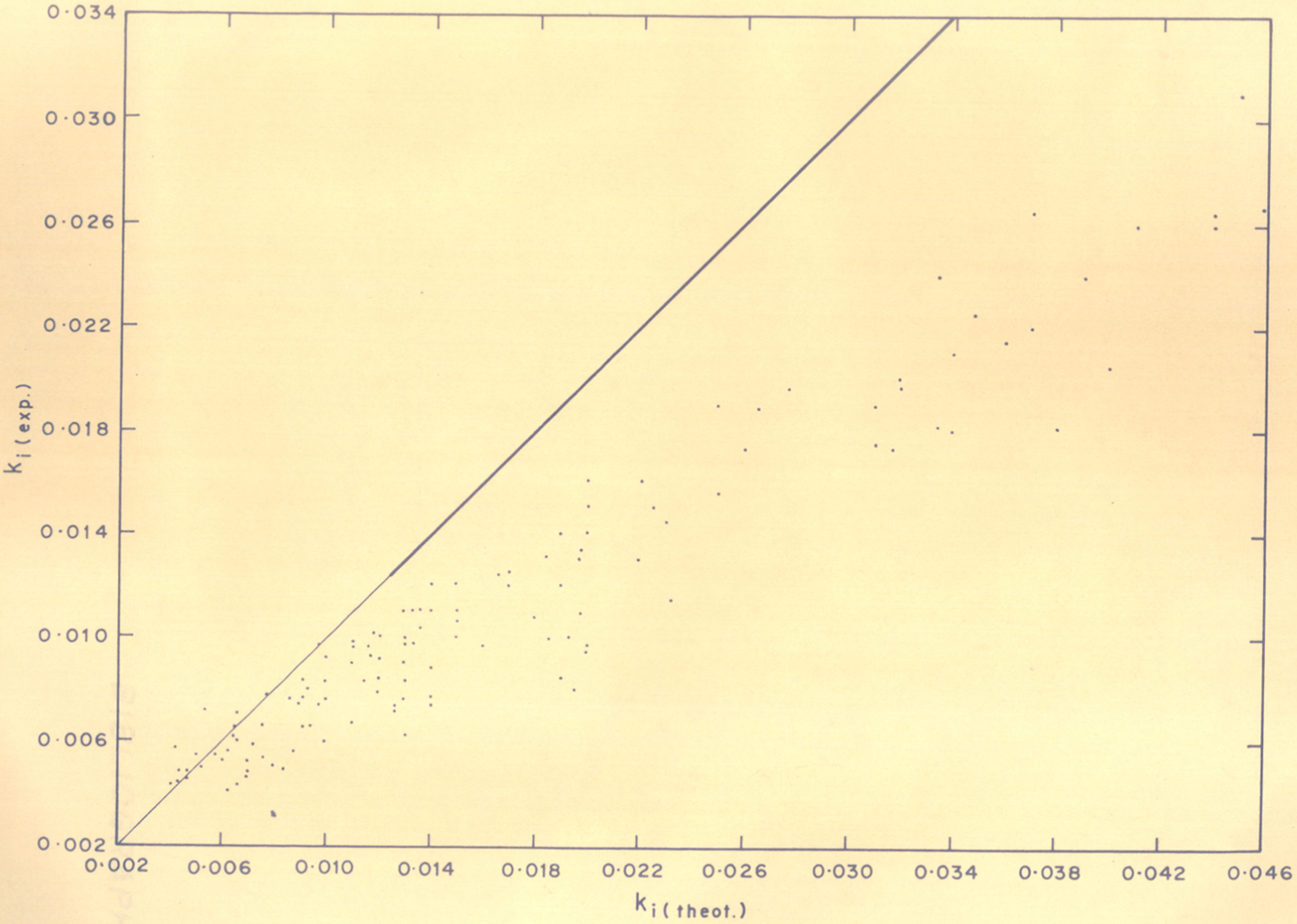

FIG. (6·1). COMPARISON OF EXPERIMENTAL AND THEORETICAL k_i VALUES.

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NOMENCLATURE

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A = Instantaneous area of mass transfer (cm.^{2})

A_{av} = Average area of mass transfer (cm.^{2})

A_n = Expansion coefficient of the n-th term

A_N = Internal cross sectional area of the nozzle (cm.^{2})

a = Radius of microwave cavity (or drop) (cm.)

$\vec{B}$ = Magnetic induction (webers/m.)

B_n = Modal constant of Equations (3.21), (3.22) *and* (3.23)

C_0)
C_1)
C_2)
C_3) = Constants of Equations (3.51), (2.43), (2.44) (2.45) and (2.46)

C' = Constant of Equations (3.24), (3.25) and (3.26)

C'' = $1/(K_o \mu_o)^{1/2} = 2.998 \, . \, 10^8$ (m./sec.)

c = Concentration (gm.mole/lit.)

c_o = Initial or inlet concentration (gm.mole/lit.)

c_1 = Actual mass transferred (gm.mole/lit.)

c^* = Equilibrium concentration (gm.mole/lit.)

$c(\eta)$ = Concentration at radial distance η from centre of circulation (gm.mole/lit.)

c_i = Inside concentration at time, t (gm.mole/lit.)

$c_{i,in.}$ = Concentration at the interface (gm.mole/lit.)

c_{io} = Inlet concentration at $t = 0$ (gm.mole/lit.)

c_t = Concentration at the end of drop formation time, t_f (gm.mole/lit.)

D = Diffusion coefficient (cm.^{2}/sec.)

$\vec{D}$ = Electric displacement (coulombs/m.^{2})

d = Instantaneous diameter of the drop (cm.)

d_N = Inner diameter of the nozzle (cm.)

E = Efficiency of mass transfer

$\vec{E}$ = Electric intensity (volts/m.^{3})

$\bar{E}'$ = Effective eddy diffusivity (cm.^{2}/sec.)

E_T = Efficiency of mass transfer defined by Equation (5.1)

E_ϕ = Azimuthal component of $\vec{E}$

$\vec{H}$ = Magnetic intensity (amp./m.)

H_o = Constant defined by Equation (3.28)

H_r = Radial component of $\vec{H}$

H_θ = Meridian component of $\vec{H}$

$\vec{J}$ = Current density (amp./m.^{2})

j = Constant of Equations (3.22) through (3.28)

K = Magnitude of wave vector; also $K = K_r K_o$ = electric inductive capacity of medium

K_o = $8.854 \cdot 10^{-12}$ (farad/m.)

K_r = Dielectric constant

k_i = Effective mass transfer coefficient (cm./sec.)

k_{i1} = Effective mass transfer coefficient for the direction of transfer from dispersed to continuous phase (cm./sec.)

k_{i2} = Effective mass transfer coefficient for the direction of transfer from continuous to dispersed phase (cm./sec.)

k_L = Liquid phase mass transfer coefficient (cm./sec.)

M = Molecular weight (gm./mole)

M_T = Net mass transferred at any time, <u>t</u>

M_∞ = Net mass transferred at infinite time

$M(t)$ = Mass of solute at time <u>t</u> in the drop

$M(o)$ = Mass of solute at time $t = 0$ in the drop

N = Net mass transferred up to time <u>t</u> (gm.mole)

N' = Diffusion flux (gm.mole/sec.cm.^{2})

N'' = Drop flux (gm.mole/sec.(single drop))

P = Pressure (kg./cm.^{2})

$P_n^1(\cos\theta)$ = Legendre function of first kind of order <u>n</u>

$P(\eta)d\eta$ = Differential probability of an elemental volume at radial distance η from the centre of circulation

p = Constant of Equation (2.7)

Q_W = Volumetric rate of inflow (cm.^{3}/sec.)

q = Constant of Equation (2.7)

r = Radius of the drop; also radial co-ordinate

r_c = Instantaneous centre of circulation

r_f = Final radius of the drop (cm.)

S = Constant defined by Equation (4.17)

t = Time (sec.)

t_c = Time of circulation along the streamline corresponding to parameter C

$t_{c\frac{1}{2}}$ = Actual time of half circulation along the streamline $\psi = C$

$t'_{c\frac{1}{2}}$ = Normalised dimensionless time of half circulation along the streamline $\psi = C$

$\bar{t}_{c\frac{1}{2}}$ = Weighted average of half-time of circulation along the streamline $\psi = C$

$\bar{t}_c$ = $2\ \bar{t}_{c\frac{1}{2}}$

t_f = Time of formation (sec.)

V = Velocity (cm./sec.)

V_N = Velocity of liquid at the nozzle (cm./sec.)

V_o = Velocity at the instantaneous centre of the drop

V_r = Radial component of velocity

V_θ = Theta component of velocity

V_ϕ = Phi component of velocity

v = Volume of the drop (cm.^{3})

x = Linear distance of diffusion (cm.); also dimensionless variable defined by Equation (3.59)

y, y' = Parameter defined by Equation (2.34); also dimensionless variable defined by Equation (4.6)

Y_n = n-th eigen function

Z = Radial displacement

$\overline{Z^2}$ = Mean squared radial displacement

$(Z_{n+\frac{1}{2}})(Kr)$ = Half integral Bessel function

Greek letters

α_1 = Constant defined by Equations (2.14), (2.18), (2.24), (2.30) and (2.36). Note : The definitions of α_1 are different in the different model equations mentioned above

α_2 = Constant defined by Equation (2.51)

α_c = Constant defined by Equation (3.68)

$\bar{\alpha}_c$ = Weighted average of α_c

β = Proportionality constant of Equation (5.17) (theoretical value : 0.01)

λ_n = n-th eigen value

η, η' = Radial distance from the centre of circulation; also a constant of Equations (3.24), (3.25) and (3.26)

μ = Viscosity (gm./cm.sec.); also = $\mu_r \mu_o$ = magnetic inductive capacity of medium

μ_c = Viscosity of continuous phase (gm./cm.sec.)

μ_o = $4 \pi \ 10^{-7} = 1.257 \ 10^{-6}$ (henry/m.)

μ_D = Viscosity of dispersed phase (gm./cm.sec.)

μ_r = Permeability

ψ = Stream function

ϕ = Phi co-ordinate

θ = Theta co-ordinate

ρ = Density of the liquid (gm./cm.^{3}); also charge density (coulombs/m.^{3})

σ = Electric conductivity (1/ohm.m.)

ω = Circular frequency of the field oscillation in microwave cavity (1/sec.)

ω' = Angular position in spherical co-ordinates (radians) (see reference (25))

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