LIQUID-LIQUID EXTRACTION BY THE SLUG TECHNIQUE

By

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ABSTRACT

The slug technique proposed by Baird and Ho[16] is a simple and easy way of obtaining the fundamental data on mass transfer coefficients in ternary liquid-liquid extraction. The technique yields a constant measurable interfacial area and the coefficients thus obtained from the experiments could be compared with those obtained by the penetration theory.

The technique, as proposed, operates on a cylindrical slug of the organic phase suspended freely by downflow of water. This is modified in this work, by means of a disc arrangement to accommodate changes in aqueous phase flow rate. It was observed that the disc, which holds the slug at the center of the tube, has also enhanced the mass transfer rates by improving the mixing inside the slug, the improvement being higher for smaller slug lengths.

The mass transfer coefficients in general were found to be lower than the penetration theory values. This could be due to any of the effects of dissolution of the solvent in the aqueous phase, hydrodynamic and surface conditions, variation of phase resistance with time, contaminants, and uncertainity about the distribution coefficient of the system: n-Heptane-Iodine-Water. Mass transfer rates in extraction with reactions were also found to be low and was thought to be due to violation of the assumption that the reaction between iodine and sodium thiosulphate is instantaneous. In the experiments with acetic acid as the solute, transfer rates were found to be higher than the expected because of Marangoni effects induced by the solute. It was concluded, however, that the technique will still be useful in obtaining the fundamental data with the use of a system with well-defined distribution data and redistilled solvents.

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[*] Refers to: Organic phase/solute transferring from the organic phase-solute or reagent transferring from the aqueous phase/aqueous phase.

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CHAPTER 1

INTRODUCTION

Liquid extraction is used to separate the constituents of homogeneous liquid mixtures by contacting with an immiscible or partially miscible solvent. The solvent makes use of solute-solvent interaction or chemical reaction.

Liquid extraction has been widely used as a separation technique for laboratory purposes. Its large-scale industrial application dates back to 1930s when it was applied to separate aromatic hydrocarbons from the kerosene fraction during oil refinery. Some of the other important applications include separation of Benzene-Toluene-Xylene from light feed stocks, acetic acid from aqueous solutions etc, effluent treatment for removal of phenol in the inorganic field, manufacture of KNO_3 and H_3PO_4, and several pharmaceutical extractions, e.g., penicillin.[1]

The development of the science of extraction started with the first step of obtaining the physical equilibrium data for various ternary systems. The data were presented in the form of triangular and Mc-Cabe Thiele diagrams. These diagrams were useful in the design of multistage extractions. The generation of the equilibrium data has been greatly facilitated with the advent of a device in Sweden, the AKUFVE mixer centrifuge. Due to its high initial cost, an alternative approach is to predict the whole equilibrium surface from limited data from thermodynamics, such as by use of NRTL equations.

Temperature usually has a pronounced effect on the equilibrium position and hence data must be obtained under isothermal conditions.

In the past couple of decades, nuclear and hydrometallurgical processes have become increasingly important and these have led to increased interest in chemical equilibria.Typical applications,inv~~ol~~ving reaction; are extraction of uranyl nitrate from aqueous solution to TBP (Tributylphosphate), extraction of malodorous merceptans from gasoline by aqueous caustic solution, hydrolysis or saponification of esters of fatty acids, copper into LIX 64N (Hydroxyoxyme), a proporietary mixture developed by General Mills Inc. The equilibrium data as obtained do not indicate the actual rate of mass transfer and its chemical-rate dependence. For this reason the treatment of mass transfer with simultaneous chemical reaction is necessary in reaction accompanied processes.

It is important to know the controlling mechanism, whether diffusionally controlled or reaction controlled or both, ~~if a~~ reaction is involved before attempting to design the necessary equipment for the processes in industry.

A number of techniques were developed over the years to study the extraction mechanisms and some were found suitable in that they give a constant and measurable interfacial area in order to be able to predict the mass transfer coefficient from rudiments[2] and then compare with the measured values. These include:

1. Quiescent cells: Lewis[3] developed a cell in which the interface is an annular area and the phases can be stirred individually at desired rates. Data were presented in the form of generalized correlations by Lewis, Mayers,[4] and Gordon and Sherwood[5] for several systems. Lewis cells have been used extensively to study turbulent mass transfer.[6,7]
2. Stirred cells with mechanically swept surface: Bakker et al.,[8] Nanda and Sharma[9] used cells in which the interface was mechanically swept by means of stirrer whose blades just touched the interface.
3. Rising drops: Many researchers have reported works on mass transfer to and from drops. These have been reviewed recently by Laddha and Degaleesan.[10]
4. Mixer-Settler Systems: Studies in mixer-settler systems have been mostly confined to

stage efficiency. Interfacial area could be calculated by means of empirical equations[11] which are limited to certain conditions and are approximate.

5. Wetted-wall contactors: In these a thin film of liquid flows down the wall under the influence of gravity and is contacted concurrently or countercurrently with the second liquid. Bakker et al.[12] devised a set up in which good control of flow conditions could be achieved.
6. Spherical-film contactor: Ratcliff and Reid[13] used an apparatus in which one liquid flowed over the sphere in a laminar film in a second immiscible liquid that was stagnant.
7. Concentric-jet: Ward and Quinn[14] among others used co-current concentric jets in which one liquid formed the core and the other liquid formed outer shell of fluid. In a recent paper yet to be published, Freeman and Tavlarides[15] proposed the liquid jet recycle reactor as a means of studying interfacial reaction in liquid-liquid systems.
8. 'Rising Slug': Perhaps the most recent technique developed to study the mass transfer was the 'rising slug' technique by Baird and Ho.[16]

They formed a stable slug of organic phase which could move freely under certain predictable conditions, in a vertical glass tube filled initially with water, and kept the slug stationary by means of water flowing down the tube. They obtained the mass transfer rates for several binary systems by noting the slug shrinkage rates and found to be in close agreement with the predicted values from Higbie' penetration theory.[2] Thus they concluded that the technique could be useful in mass transfer studies of reaction - accompanied extraction.

The work of Baird and Ho was concerned mainly with the development of the technique and its applicability to binary liquid-liquid systems - 1-Butanol-water, MIBK-water, and 1-pentanol-water. The systems were studied at a single continuous phase flow rate which could hold the slug stationary. Another recognizable fact is that all the systems they worked with had small interfacial tension at the operating temperature. Thus any chances of contamination and its effects were absent.

In this work, the technique is used to study mass transfer in ternary liquid-liquid systems. With slight modification the technique could be used to study the effect of change in continuous phase flow rate which was not possible in the earlier set-up. Further, the system studied has large interfacial tension. Mass transfer accompanied by reaction was looked at in a few cases.

CHAPTER 2

BASIC PRINCIPLES

2.1 Fluid Mechanics of Slug Flow

The slug flow behaviour in gas-liquid systems, reviewed by Wallis,[17] has been applied to liquid-liquid systems by Baird and Ho.[16] They found that liquid-liquid slugs were stable and laminar in vertical tubes in the so-called "capillary regime" in which the relative velocity of the slug was governed by interfacial tension and gravity forces.

Velocity-profiles in slug flow

The important and necessary assumptions in the calculation of velocity profiles[16] are that the organic and aqueous phases are in laminar flow, fully developed and axially symmetric. Since the end effects viz., the tail and nose are neglected, the derivations will be strictly valid for large length/diameter ratios.

The steady-state velocity profiles are obtained by solving the Navier-Stokes equations for each phase with the appropriate boundary conditions. The equation for each phase reduces to

$$P' - \rho g = (\mu/r) \frac{d}{dr}\left(r \frac{dv}{dr}\right) \qquad (1)$$

where $P' = \frac{dp}{dz}$; the positive Z directs vertically down. Successive integrations give

$$\left(\frac{P' - \rho g}{\mu}\right) \frac{r^2}{2} = r \frac{dv}{dr} + U_1 \qquad (2)$$

$$\left(\frac{P' - \rho g}{\mu}\right) \frac{r^2}{4} = v + U_1 \ln r + U_2 \qquad (3)$$

The boundary conditions applicable to the two phases are:

a. Organic phase velocity reaches a maximum at the center of the tube $\frac{dv_o}{dr} = 0$ @ $r = 0$ (Tube center)

b. Aqueous phase $v_a = 0$ @ $r = R$ (Tube wall)

c. At interface $v = v_i$ @ $r = R_i$

d. At interface, shear stresses exerted by each phase are in balance $\mu_a (\frac{dv}{dr})_i = \mu_o (\frac{dv_o}{dr})_i$

These boundary conditions were used by Baird and Ho[16] in the solution of Eqn. (3) to give an expression for the dimensionless radius ϕ for a slug held in a fixed position by downflow of water:

$$\frac{8\mu_a v_f}{R^2 (\rho_a - \rho_o) g} = \frac{(\phi^2\psi - 4\phi^4 \ln \phi)(2\phi^2 - 1 - \phi^4)}{(2\phi^4 - 2\phi^2 - \psi\phi^4)} + 2\phi^4 - 2\phi^2 - 4\phi^4 \ln\phi \qquad (4)$$

The left hand side can be calculated from the measured values of v_f, tube diameter, and system properties. Viscosity ratio ψ is also known and hence dimensionless slug radius ϕ can be found. Since the equation contains ϕ implicitly, a small computer programme[18] is used to

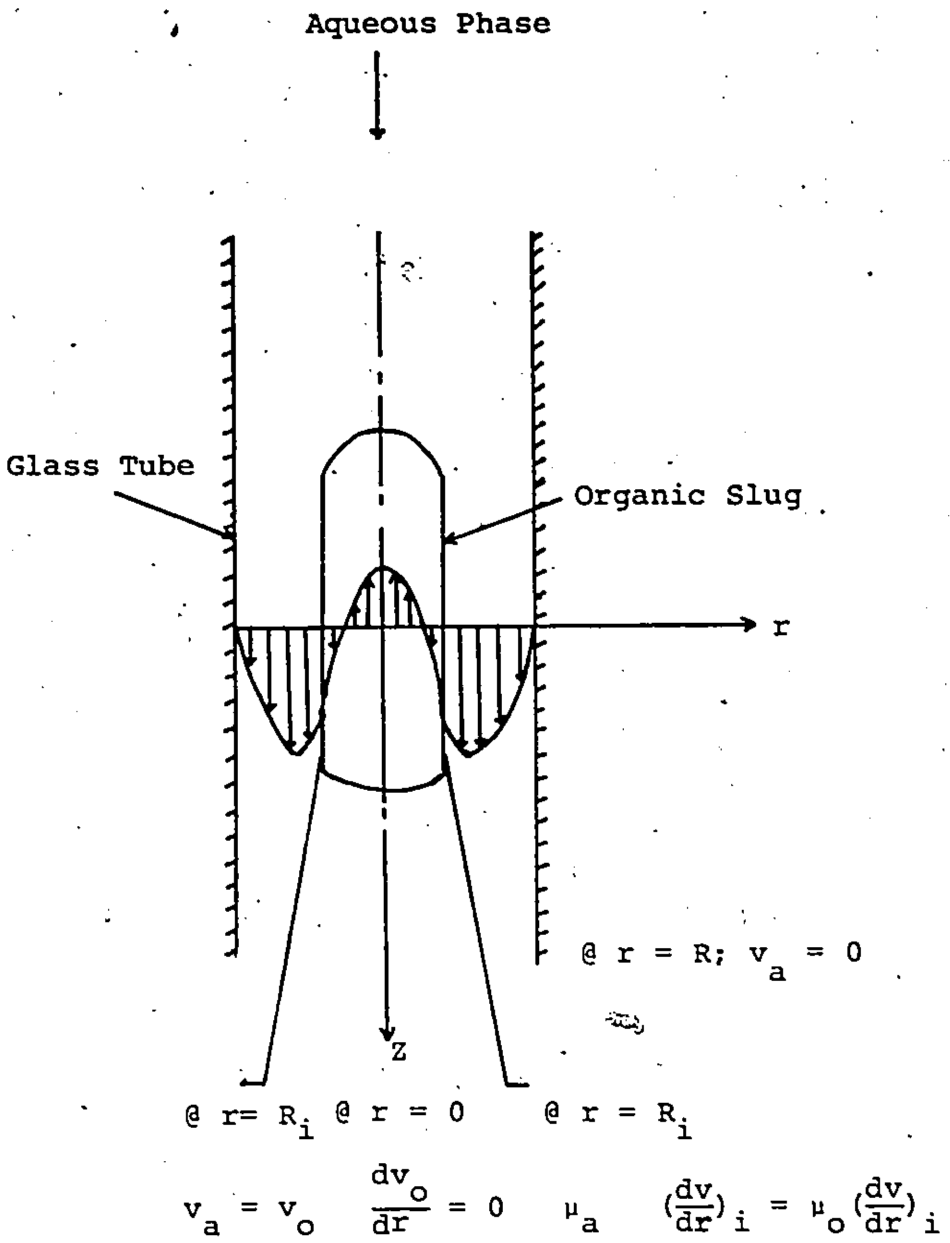


FIGURE 1 Velocity Profiles and Boundary Conditions (not drawn to scale)

solve for ϕ. A second equation, rather similar to Eqn. (4) was given for the case of a freely rising slug in stagnant water. The interfacial velocity in the former case can be calculated by the equation:

$$V_i = \frac{R^2(\rho_a - \rho_o) g \, \phi^2 \ln \phi}{2 \, \mu_a} \quad \frac{\phi^2(\phi^2 - 1)}{2(2\phi^2 - 2\phi^2 - \psi\phi^4)} + 1 \qquad 4(a)$$

2.2 Prediction of Mass Transfer by Penetration Theory

The contact time $\tau (= L_s/V_i)$ in all the present experiments, also as had been reported by Baird and Ho,[16] is of the order of 1 second. The annular aqueous film has a thickness of about one tenth of a tube radius or 600 μm. Since the penetration distance ($\sqrt{D\tau}$ = 30μm) is very small compared to the aqueous-film thickness, the simple "semi-infinite" penetration model developed by Higbie[2] can be used and the mass transfer coefficient is given as

$$k = 2(D/\pi\tau)^{1/2} = 2(DV_i/\pi L_s)^{1/2} \tag{5}$$

The rate of mass transfer, $\dot{m}$, of any component is calculated based on the cylindrical side area of the slug with the end effects being neglected.

The rate of transfer of a component from either phase is given by $N_A = (C^* - C_b) K_L \ A_s$ (6)

$$= V_s \frac{dc_s}{dt} \tag{7}$$

If the organic phase is depleted of its dissolved component, $\frac{dc_s}{dt}$ will be negative, otherwise positive.

2.3 Special Hydrodynamic Effects

2.3.1 Stagnant Layer

Treybal[11] has summarized some of the reasons for low mass transfer rates. He included the effects of blocking of the surface, rigidity of the surface, and interaction of adsorbed substances and extracting solute under the general heading of "interfacial resistance due to adsorbed trace substances".

Though these effects might play an important role in the presence of surface-active agents[19-21], they may be equally applicable in the presence of trace impurities which are inevitably present in the liquids.

It has been suggested[22] that the surface active materials are dragged along the usually mobile liquid-liquid interface to the downstream side, thereby causing an interfacial tension gradient along the surface that opposes the flow of the surface and makes the surface more rigid. This in turn reduces the transmittance of the turbulence from one fluid to the other across the interface and hence the mass transfer coefficients to well below the expected values. An interfacial tension gradient can act against the shear stress at the interface as shown in Fig. 2, affecting the boundary condition (d) given in Section 2.1.

The boundary condition modifies to:

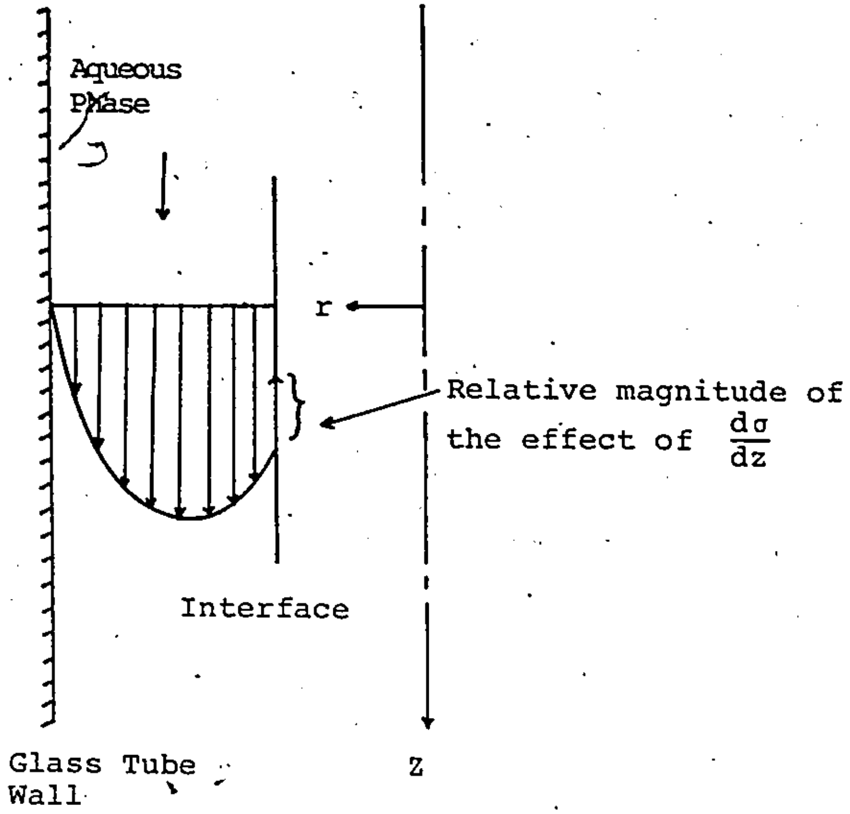


FIGURE 2 Effect of Surface Tension Gradient at Interface on Velocity (not drawn to scale)

$$\mu_a \frac{dv_a}{dr}\bigg|_i = \mu_o \frac{dv_o}{dr}\bigg|_i - \frac{d\sigma}{dz} \qquad (8)$$

West et al.[23] had observed that passing benzene through Tygon tubing dissolved sufficient surface-active plasticizer to reduce the rate of extraction greatly. These effects will be referred to again in Chapter 7.

2.4 Interfacial Rippling and Turbulence

Three general types of phenomena were observed by Sherwood and Wei[24] at the liquid-liquid interfaces in static conditions for number of systems: rippling and oscillation of the interface, transparent streams and small drops leaving the interface, and opaque streams resulting in spontaneous emulsification. Davies[25] defines the mechanism of this spontaneous emulsification as that of "diffusion and stranding" for the system benzene-acetic acid-water. Benzene initially tries to dissolve in water in the presence of solute but with the transfer of solute forms an emulsion. Davies and Rideal[26] claim that there has not yet been found a system where spontaneous emulsification is not present during the transfer of a third component. Lewis[27] and Pratt[28] observed ripples, erratic pulsations and surface motion of drops while measuring the interfacial tension by pendant drop method. These effects were also observed during mass transfer with reaction and were thought to increase the rate of solvent extraction.

Interfacial turbulence is a result of the differences in concentrations and temperature along the interface and hence differences in interfacial tension. This is the well-known Marangoni effect. The surface instability or turbulence is usually associated with the transfer of a solute and its direction of transfer. Sternling and

and Scriven[29] carried out a detailed analysis of the surface turbulence using their 'roll cell model'. It was concluded that interfacial instability is usually promoted by transfer of solute into phase of lower viscosity, higher diffusivity, and by larger differences in kinematic viscosity and solute diffusivity between the two phases, steep concentration gradients and low viscosities and diffusivities of both phases. However, as suggested by Bakker et al.,[12] interfacial turbulence cannot occur in binary systems since the phases would be mutually saturated along the interface. Thus interfacial tension will be same practically everywhere provided the temperature remains constant.

2.5 Addition of Mass Transfer Resistances

According to the Whitman's[30] two-film theory, the overall resistance to the transfer of a solute from one phase to another is the sum of the individual phase resistances. The two major postulates used, however, are the equilibrium comparable to static equilibrium at the interface and the presence of "very narrow" thin laminar films at the interface. Treybal[11] has given the general method of calculating the overall transfer coefficient from individual phase coefficients. The final equations are summarized below for later reference.

Solute transferring from aqueous to organic phase:

$$\begin{aligned} N_A = \text{mass transfer rate} &= K_o(C_o^* - C_o) \\ &= k_o(C_{oi} - C_o) \\ &= k_a(C_a - C_{ai}) \\ &= K_a(C_a - C_a^*) \end{aligned} \qquad (9)$$

After rearrangement, $\frac{1}{K_a} = \frac{1}{k_a} + \frac{1}{mk_o}$

$$\text{or} \quad \frac{1}{K_o} = \frac{1}{k_o} + \frac{m}{k_a} \qquad (10)$$

where 'm' = $[C_a/C_o]_{eqm}$.

Solute transferring from organic to aqueous phase:

$$\begin{aligned} N_A &= K_o(C_o - C_o^*) = k_o(C_o - C_{oi}) = k_a(C_{ai} - C_a) \\ &= K_a(C_a^* - C_a) \end{aligned} \qquad (11)$$

Again, Eqn.(10) is obtained upon rearranging Eqn. (11). It has been tacitly assumed above that no reaction is taking place during the course of mass transfer. However, if there is also a reaction, similar analysis will give

$$\frac{1}{K_o} = \frac{1}{\varepsilon_o k_o} + \frac{m}{\varepsilon_a k_a} + \frac{1}{k_i} \qquad (12)$$

The liquid phase resistances are usually larger by an order of magnitude than the interfacial resistance. The effect of chemical kinetics is to increase resistance through k_i or to reduce resistance by enhancing k_a or k_o. Interfacial resistance will also be affected by the presence of the stagnant layer as explained in the last section.

In experiments with wetted-wall tower, Brinsmade and Bliss[31] resolved the overall coefficient into individual coefficients by empirical means. They assumed the k_o and k_a to be functions of the flow rates of the phases in contact and fit the experimental data. Murdoch and Pratt[32], on the same lines, included an interfacial resistance term to account for the reaction. Recently Rod[33] has reviewed the literature for time-dependent resistances in both phases between a drop and an ambient liquid. He presented, for the case of comparable resistances in both phases, the time-varying resistance inside the drop as a product of the limiting resistance, for no resistance in the continuous phase, and a correction factor which is a function of the contact time.

CHAPTER 3

EXPERIMENTAL ASPECTS

3.1 Apparatus

3.1.1 Free-Slug Apparatus

This apparatus is basically of the same form as described by Baird and Ho[16] except for small changes as given below and shown in Fig. 3.

The apparatus consists of a long glass tube of 1.26 cm I.D. which was preferentially wet by the running aqueous phase. The main section of the tube (excluding the end portions) measured 60 cm long whereas the end sections were each tapered (tapering angle less than 7°) to a length of 5 cm ending in a diameter 4 mm I.D. The tapering at the bottom helped in getting the slug liquid sucked gradually thus preventing from breaking into finer droplets. The tapering at the top was kept mainly to allow the aqueous phase flow pattern to become fully developed before contacting the slug. This has also helped in maintaining the slug stationary. The top of the tube was formed into a T-section of which one passage was connected to the ejector with a needle valve 'A' in between. The second tube was connected to a copper tube having a needle valve 'D' which inturn was connected to two copper tubes, fitted with needle

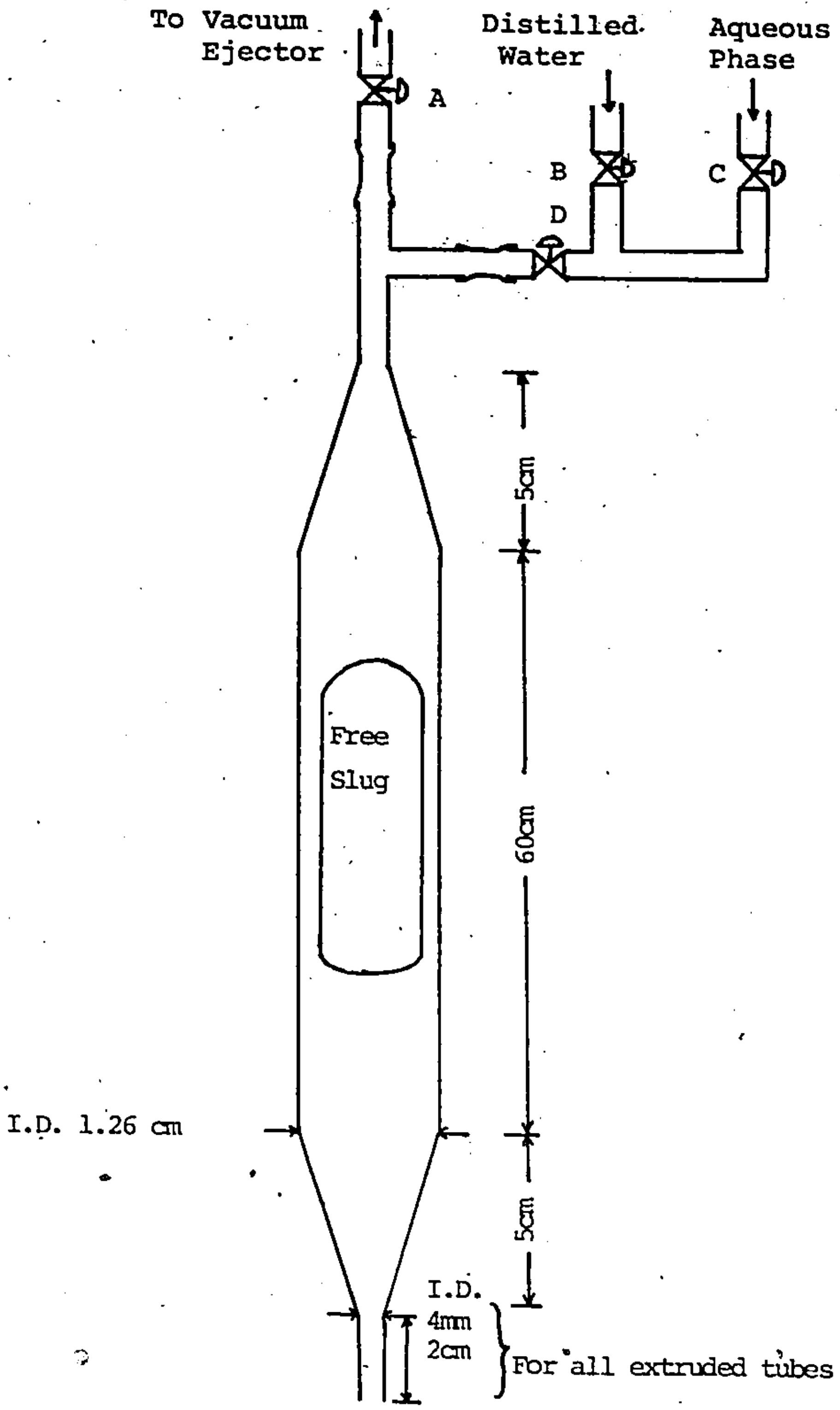


FIGURE 3 Free-Slug Apparatus (not drawn to scale)

valves 'B' and 'C'. The latter were connected to two overhead reservoirs (not shown in the figure) of capacity ranging from 15 to more than 20 litres.

3.1.2 Modification with Disc

The arrangement described in the earlier section has a serious disadvantage. For any given length of slug of the same fluid, the flowrate of the aqueous phase could be maintained only at that value for which the slug was held stationary. Any alteration in the flow rate of continuous phase resulted in upward or downward movement of the slug. To circumvent this problem, a small disc-type arrangement was constructed as shown in Fig. 4.

The disc apparatus was constructed of glass, stainless steel (S.S) and teflon. The outer glass-tube was 1.24 cm I.D. and 30 cm long. It has two side openings, 20 cm apart: one connecting to the ejector and the other connecting to two reservoirs as described earlier. The top of the tube was closed with a rubber stopper through which passed a S.S. tube of 1/8" O.D. concentric with the glass tube. The lower end of the S.S. tube was snugly fit into perforated circular plates of S.S. (2 mm thick) and teflon (1 mm thick), each with a diameter of 1.15 cm. Teflon was used as the bottom plate so as to be wetted by the organic fluid. The two plates were joined together by an epoxy glue.

It was important that the slug formed beneath the stainless steel/Teflon disc should be symmetrical, so the disc was centered by means of a 1 cm long Teflon cylinder, fitting snugly inside the 1.24 cm diameter outer tube. The Teflon

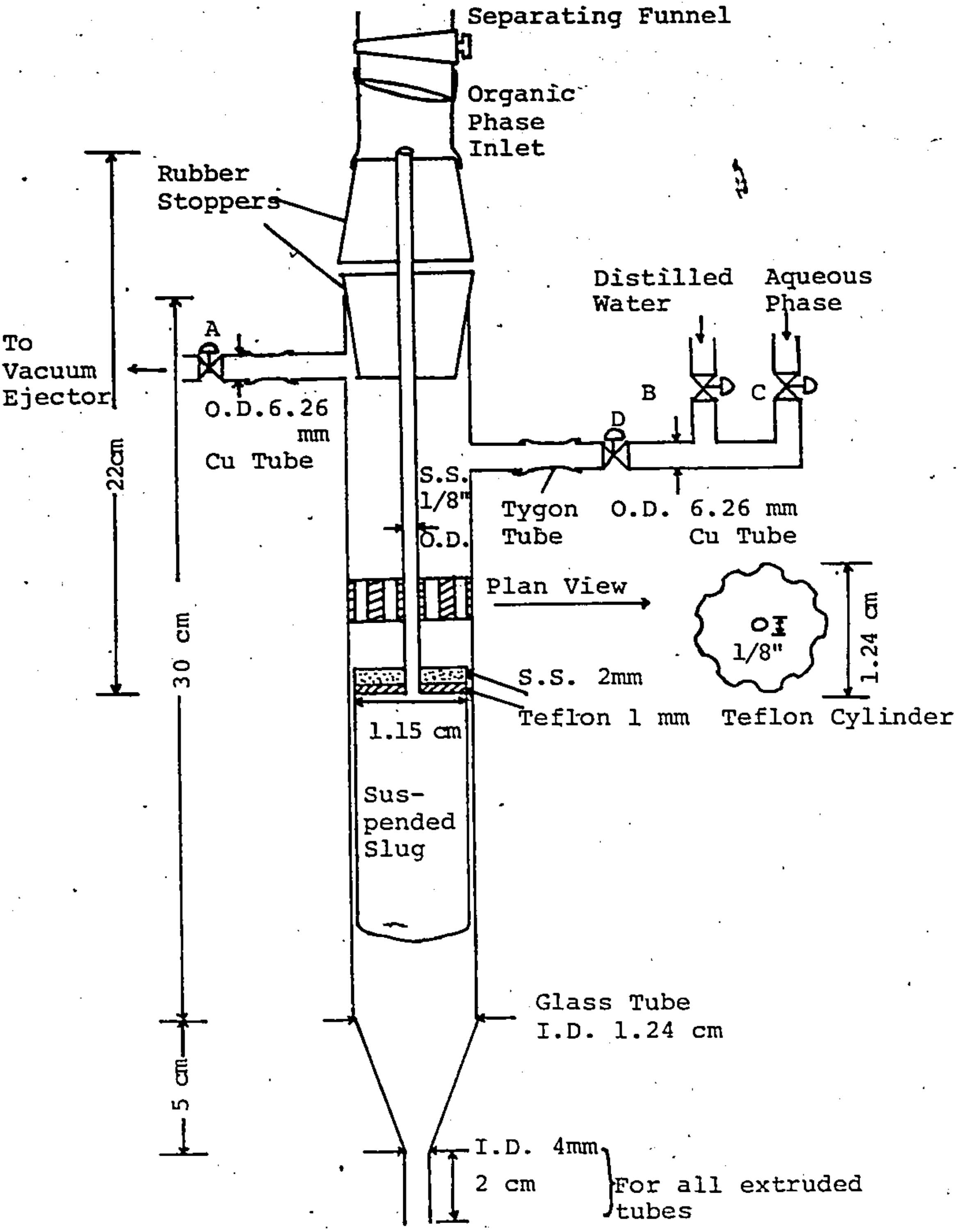


FIGURE 4 Disc-type Apparatus (not drawn to scale)

rod was attached to the S.S. tube by means of a grub screw and was situated at 4-5 cm from the disc. It was provided with semi-circular longitudinal slots to permit the flow of aqueous phase.

The top projecting end of the S.S. tube was fitted with an inverted rubber stopper which was connected by means of a short tygon tube to a separating funnel. The latter contained the organic liquid to be introduced through the S.S. tube and be suspended from the disc during the course of the experiment.

3.2 Systems Studied

Most of the experiments were carried out with n-Heptane (J. T. Baker Chemical Co., Pa.) as the organic liquid and Kerosene (Fisher Scientific, N.J.) was used in the preliminary studies. Likewise, Iodine (B.D.H. Laboratory Reagent, Resublimed) was the transferring solute in many of the experiments. In experiments involving a reaction, sodium thiosulphate (Anhydrous, Fisher Scientific, N.J.) was present in the aqueous phase. Acetic acid (Reagent A.C.S. grade, Fisher Scientific Co., Ltd.) was also used as solute in some of the experiments. The series of experiments carried out with the corresponding solute, solvent, direction of transfer and the variables in study are recorded in Table 1. The ranges of physical properties and Reynolds number studied are presented in Table 2. The pH of the distilled water used in the experiments was 7.3.

TABLE 1 DETAILS OF THE EXPERIMENTS

Series No.	Length of Slug cm.	Aqueous Phase Flow Rate (v_f) cm/s	Organic Phase	Aqueous Phase	Solute and Direction	Disc Used
1	3.0- 6.1	1.761-2.6	Kerosene	$Na_2S_2O_3/H_2O$	I_2;Org.→Aq.	No
2	4.7-11.3	1.1493-2.339	"	water	A.A;* "	"
3	3.0	1.0769	"	"	I_2;Aq.→Org.	"
4	3.0-9.0**	2.294-3.5243	n-Heptane	"	I_2; "	"
5	6.0	3.0723	"	$Na_2S_2O_3/H_2O$	I_2;Org.→Aq.	"
6	3.0-12.0**	0.6389-3.074	"	water	I_2; Aq.→Org.	Yes
7	6.0	1.094-2.872	"	"	I_2;Org.→Aq.	"
8	6.0	3.206	"	$Na_2S_2O_3/H_2O$	I_2; "	"
9	6.0	1.3621	"	water	A.A.*; "	"

*A.A. - Acetic Acid.

**In steps of 3 cm.

TABLE 2 RANGE OF PHYSICAL PROPERTIES AND REYNOLDS NUMBER

Physical Property at 20°C±1.0	Value or Range
ρ kgm^{-3} [a]	
Distilled Water	998.23
Kerosene	787.68
n-Heptane	680.20
Aqueous Phase	998.4-1019.7
Organic Phase	680.2-788.9
μ m.Pa.S [b]	
Distilled Water	1.01
Kerosene	1.4016
n-Heptane	0.42
Aqueous Phase	1.01-1.077
Organic Phase	0.42-1.4718
σ $mN.m^{-1}$ [c]	
Distilled Water	70.4
n-Heptane	19.4
Acetic acid/n-Heptane	21.3
Water - n-Heptane	43.4
D m^2S^{-1} [d]	
Aqueous Phase	1.108×10^{-9}- 1.109×10^{-9}
Organic Phase	1.3977×10^{-9}- 3.9022×10^{-9}
Re [e]	41-203

[a] For water taken from Perry and Chilton[34]. Other liquids measured.

[b] For water taken from Perry and Chilton[34]. Other liquids measured by Capillary method.

[c] Measured at 18.5°C using Fisher Autotensiomat and corrected to 20°C.

[d] Calculated using Wilke-Chang correlation.[34]

[e] Based on aqueous phase through the annulus.

3.3 Procedures

3.3.1 Start Up

The start up procedure of both types of apparatus had been almost identical. The overhead reservoir connected to needle valve B (Figs. 3,4) was always filled with distilled water (D.W.) from the laboratory supply. The second reservoir was filled with the made up solution of aqueous phase other than water.

To begin with, the glass tube was thoroughly cleaned with chromic acid and washed with D.W. Then valve A was kept open simultaneously turning on the ejector. A 250 beaker containing D.W. was placed near the exist end of the tube and water was sucked into glass tube filling up the space. Also, precaution was taken to eliminate the presence of any air bubbles in the tubes leading to reservoirs. Now, when the valve A was closed water could not flow down because diameter of the tube (4 mm) was small enough to prevent air entering by 'capillary effects'.

To form the slug in the disc-free apparatus (Fig. 3) the above procedure was repeated except that, now a beaker containing the organic liquid was kept beneath the tube. Precaution was taken to see that no air bubbles were attached to the slug which otherwise would buoy up the slug faster. The slug was then held stationary by opening valve B and adjusting the water flow rate. Any excess liquid of the slug was removed by means of a hypodermic while adjusting the position of the slug at the same time.

It was easier to form a slug in the disc-type apparatus. As before, the glass tube was filled with water at the beginning. But air was locked in the S.S. tube by doing so. By opening Valve B slightly, closing the bottom of the tube with thumb and opening the separating-funnel stopper water slowly displaced the air. Next, water from the reservoir was allowed to flow down the tube and the organic liquid was gradually introduced until the desired slug length was attained.

After the slug was formed, Valve C was opened allowing the aqueous phase to come in contact with the slug while closing the Valve B. The lag time for the aqueous phase to contact the slug was noted in each case by running a colored solution (food color dye in water). After the elapse of a prechosen time interval, aqueous phase flow was stopped and the organic phase was withdrawn by means of the hypodermic to determine its concentration. Again, a fresh slug was formed and the procedure was repeated. The experiment was continued until a sufficient number of observations were made.

3.3.2 Sampling Methods and Analytical Techniques

The organic phase iodine concentrations were determined with a Fisher electrophotometer using a green filter (5250 A^{o}). The cuvettes required 25 ml of the colored solution. Slug liquid withdrawn was thus diluted to 25 ml and its percentage absorbance was measured against pure liquid. If the slug liquid is colorless, as in the case of acetic acid (series 9, p. 27) 5 ml of it was shaken with 20 ml of water in a stoppered conical flask for 1-2 hrs. Water layer was analyzed for the amount extracted by titrating with 0.01 N NaOH solution with phenolphthalein as indicator. Concentration of the organic phase was calculated using the partition coefficient which was obtained by repeating the above procedure with a solution (organic phase) of known concentration. But, for series 2 (Table 1, p. 27) the flowing aqueous phase was collected at certain intervals of time and the concentration was determined by titration.

CHAPTER 4

MASS TRANSFER EXPERIMENTS AND THE RESULTS WITH FREE-SLUG APPARATUS

Table 1 (p. 27) has listed the various series of experiments with the variables and systems studied, and the presence or absence of the disc. As mentioned in the table, most of the experiments, carried out in the free-slug apparatus were with kerosene, mainly for two reasons: the experiments were used as a preliminary evaluation and secondly, to find its applicability as a solvent for further experiments.

4.1 System: Kerosene/Iodine - Sodium thiosulphate/Water

The transferring solute was iodine, the organic solvent was kerosene and, the second reagent was sodium thiosulphate in the aqueous phase. It was assumed that the reaction between iodine and sodium thiosulphate was instantaneous and takes place at the interface. This seems reasonable inasmuch as the aqueous side film is constantly replaced by fresh solution of the aqueous phase.

Calculation of mass transfer coefficient

The estimation of mass transfer coefficient is simple when the above assumptions hold. It was mentioned earlier (Section 2.4) that the effect of chemical kinetics is to increase resistance through k_i or to reduce resistance by enhancing k_a or k_o. In the present situation, k_1 approaches infinity and since the reaction takes place at the interface, Eqn. (12) reduces to:

$$\frac{1}{K_o} \doteq \frac{1}{k_o} \qquad (13)$$

Also, from Eqns. (7) and (11),

$$N_A = v_s \frac{dc_s}{dt} = K_o(C_s - C_s^*)A_s \qquad (14)$$

Eliminating K_o between the two,

$$\begin{aligned} v_s \frac{dc_s}{dt} &= k_o A_s (C_s - C_s^*) \\ &= k_o A_s C_s \qquad (\because\ C_s^* = \frac{C_a}{m} = \frac{o}{m} = 0) \qquad (15) \end{aligned}$$

Integrating the above equation with the initial condition $C_s = C_{s,o}$ at $t = 0$, to get

$$\ln(C_s/C_{s,o}) = \frac{k_o A_s t}{v_s} \qquad (16)$$

The experiment was carried out for two different slug lengths - 3 and 6 cms. - for the same initial concentration in the organic and aqueous phases. The photometer calibration curve for the iodine-kerosene system is given in Fig. 5. Concentration (log) versus time curves for the two slug lengths are shown in Fig. 6. The actual and

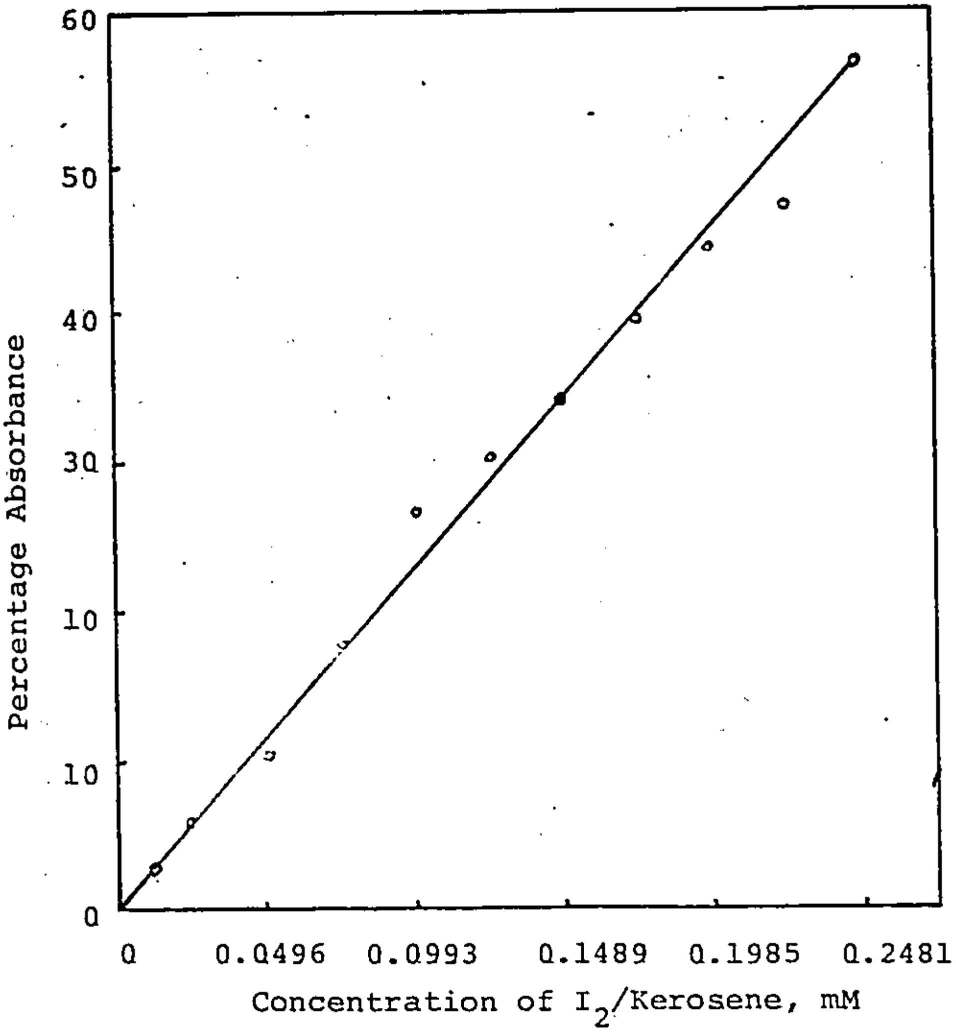


FIGURE 5 Photometer Calibration Curve for I_2/ Kerosene at 5250A°

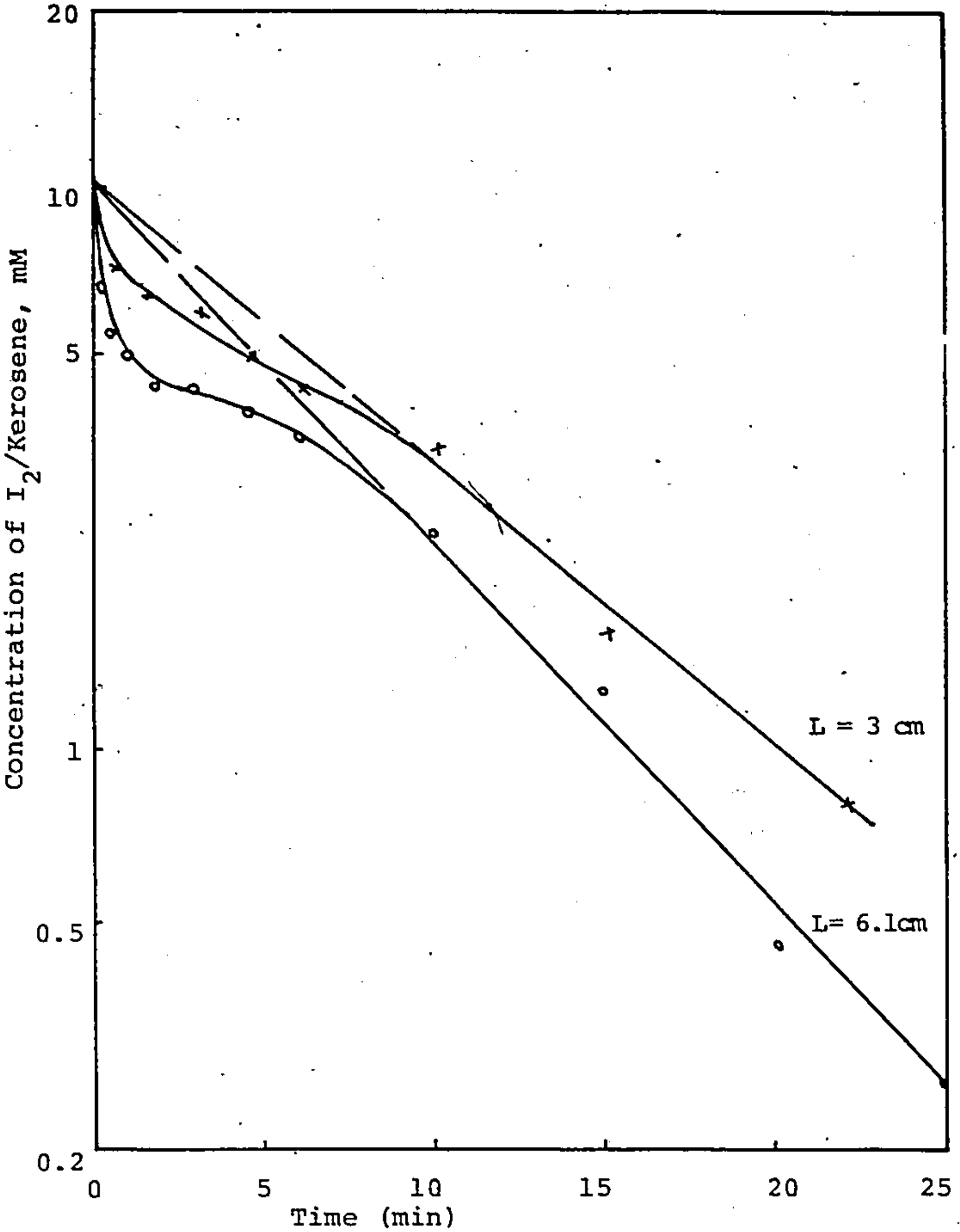


FIGURE 6 Concentration (log) vs Time for Kerosene/ I_2-$Na_2S_2O_3$/H_2O

predicted mass transfer coefficients (k_o) are given in Table 3 along with other data. Concentration - time data are also given in Appendix A.

TABLE 3 KEROSENE/IODINE - SODIUM THIOSULPHATE/WATER

Characteristic[a]	Value for L = 30 mm	Value for L = 61 mm
v_f	0.026 m/s	0.0176 m/s
v_i	0.2055m/s	0.1633 m/s
ϕ	0.9114	0.9240
k_o - Experiment		
Straight-line drop	0.5475×10^{-5} m/s	0.279×10^{-5} m/s
Initial drop	3.804×10^{-5} m/s	7.493×10^{-5} m/s
k_o - Penetration theory	11.04×10^{-5} m/s	6.902×10^{-5} m/s

[a] For explanation, see Nomenclature.

4.2 System: Kerosene/Acetic Acid-Water

This set of experiments was designed solely to understand the organic phase and its importance as solvent. For this reason, the system was so chosen to have negligible resistance for transfer in the aqueous phase thereby having the entire resistance within the organic phase.

The transferring solute was conveniently chosen to be acetic acid transferring from kerosene phase to water. The experiment was carried out for two different slug lengths - 4.7 and 11.7 cms - for the same initial concentration in the organic phase. It can be seen once again that to study a different aqueous phase velocity, a different slug length had to be chosen, notwithstanding the effect of slug length itself in the experiment. The aqueous phase velocities were different because of difference in volumes of the slugs. The variation of slug concentration with time (semi-log) for $L = 4.7$ cm is shown in Fig. 7 and for $L = 11.7$ is shown in Fig. 8. Data are also given in the appendix. The actual and predicted mass transfer coefficients are given in Table 4 with other data.

Calculation of mass transfer coefficient

Let the volumetric flow rate of the aqueous phase be q and C_a be its exit concentration. If v_s and A_s are the volume and surface area of the slug respectively, then:

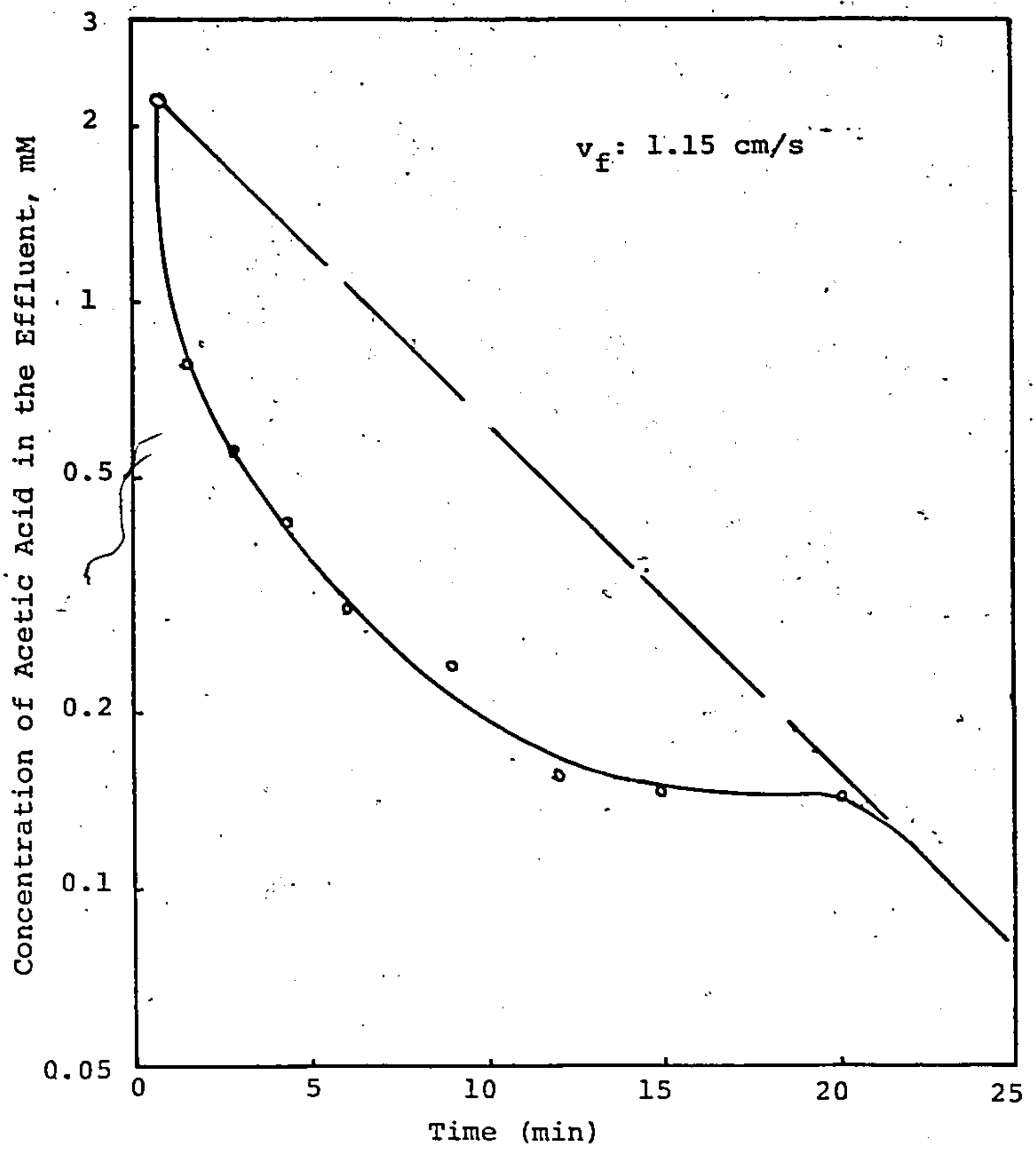


FIGURE 7 Concentration (log) vs Time for L = 4.7 cm for Kerosene/Acetic Acid-Water

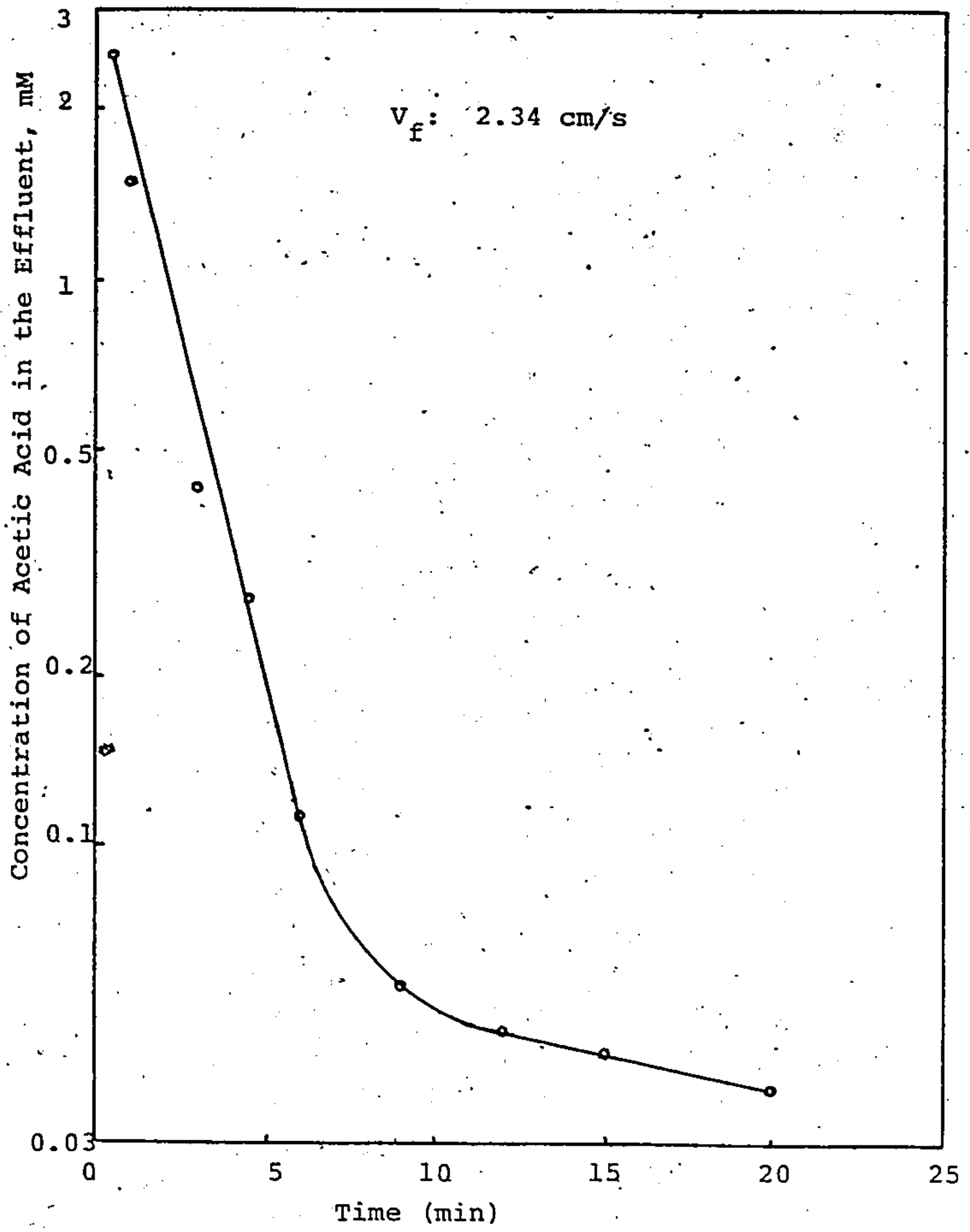


FIGURE 8 Concentration (log) vs Time for L = 11.7 cm for Kerosene/Acetic Acid-Water

$$\text{Rate of mass transfer} = qC_a = -v_s \frac{dc_s}{dt}$$

$$= A_s K_o (C_s - C_s^*)$$

But, $C_s^* = (0 + C_a)/2\bar{m} = 0$ ($\because$ m is very large)

$\therefore\ K_o \doteq k_o$

Hence $q\ C_a = -\ v_s \dfrac{dc_s}{dt} = A_s k_o C_s$.

Integrating the second equality to obtain

$$C_s = \text{constant.}\ \exp\,[-A_s k_o t/v_s] \quad (17)$$

Therefore, from the first equality

$$q\ C_a = (A_s k_o)\,(\text{constant})\ \exp\,[-A_s k_o t/v_s] \quad (18)$$

The effluent concentration versus time gives a straight line on semi-log scale the slope of which equals $(A_s k_o/v_s)$. Knowing A_s and v_s from calculated ϕ, the value of k_o could be obtained. V_i and ϕ could be obtained by solving iteratively Eqn. (4).

MASS TRANSFER COEFFICIENTS - EXPERIMENT AND THEORY

TABLE 4 KEROSENE/ACETIC ACID - WATER

Characteristic	Value for L=47 mm	Value for L=117 mm
v_f	0.0115 m/s	0.0234 m/s
v_i	0.1434 m/s	0.1915 m/s
ϕ	0.9278	0.9136
k_o - Experiment		
Straight line drop	0.6764×10^{-5} m/s	2.7086×10^{-5} m/s
Initial drop	7.558×10^{-5} m/s	4.89×10^{-5} m/s
k_o - Penetration theory	7.95×10^{-5} m/s	5.823×10^{-5} m/s

4.3 System: Kerosene-Iodine/Water

These experiments were carried out to further the understanding of the mass transfer inside the slug. The resistance was comparable on both sides of the interface. The aqueous phase was iodine in water and the organic phase was Kerosene. Iodine was slightly more favourable to the organic phase thus making the distribution coefficient (concentration in the organic phase to concentration in the aqueous phase) greater than one.

In the earlier series it was observed that the actual mass transfer rate was much less than the predicted rate. Thus, it was thought mixing inside the slug by external means could enhance the mass transfer rate. Mixing was done by occasional stirring with a hypodermic needle to which were soldered along its length small protruding knobs. The variation of concentration with time is plotted in Fig. 9 for the same slug length of 3 cm with and without external mixing ($v_f = 0.0108$ m/s). As Kerosene was found to be not a good solvent, and also since it has no well-defined composition, it was not attempted to obtain the distribution data.

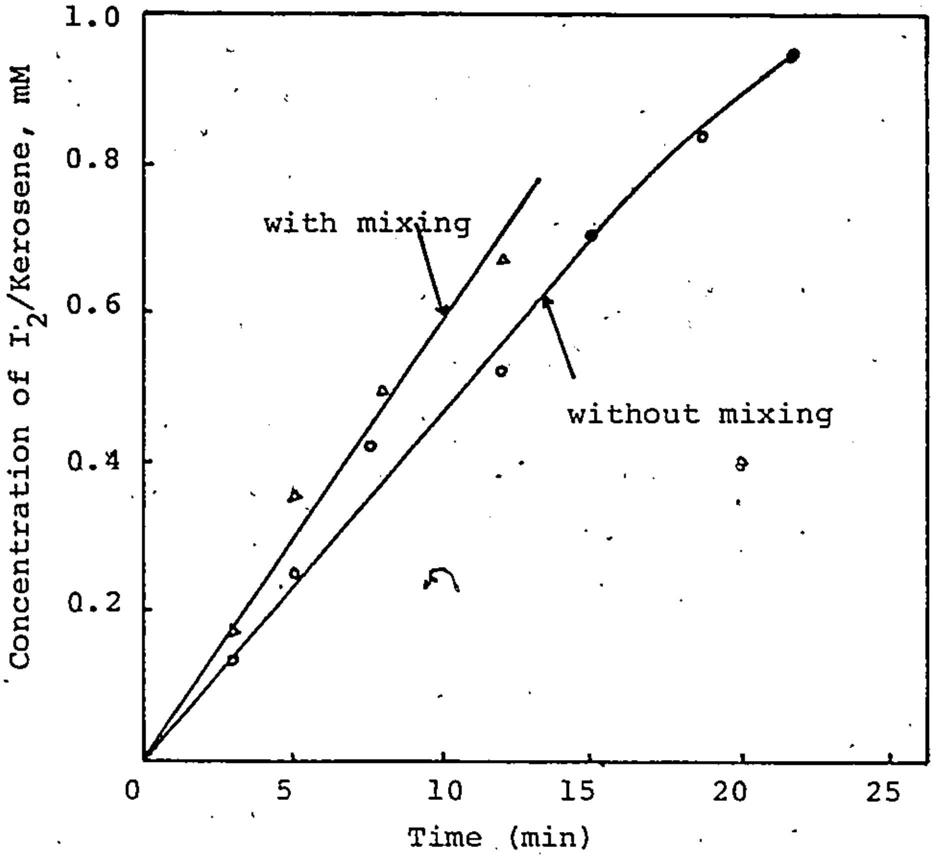


FIGURE 9 Concentration vs Time for Kerosene-Iodine/Water, with mixing and without mixing (external) inside slug

4.4 System: n-Heptane-Iodine/Water

It was concluded with the earlier series of experiments that Kerosene was not a good solvent. Because of this, n-Heptane was chosen as the solvent for reasons of low density, low viscosity, low vapor pressure and unwetting the glass tube. Also it has good solubility of iodine. The solvent n-Heptane was supplied by J.T. Baker Chemical Co. and was at least 98% pure. Photometer calibration curve for Iodine/n-Heptane at 5250A° is shown in Fig. 10.

The distribution data for the system n-Heptane-Iodine Water were obtained for several phase ratios and several concentrations. It has to be noted that phase ratio should not affect the distribution coefficient of slute between the phases. However, iodine undergoes a reversible chemical reaction with water to a negligible extent (K = Equilibrium Constant = 3×10^{-13})[32] and this is affected to some extent by phase ratio. Hence the true distribution coefficient corresponds to phase ratio where a large excess of aqueous phase is present as in the experiments. The data are plotted in Fig. 11 and the curve is extrapolated to give m = 9.412 corresponding to $v_o/v_a \to 0$. With a trial run, it was found in fact that the ratio of concentration in the slug after a sufficiently long time to the concentration of the aqueous phase was 8.85 which is close to the extrapolated value. Thus a value of 9.412 was used

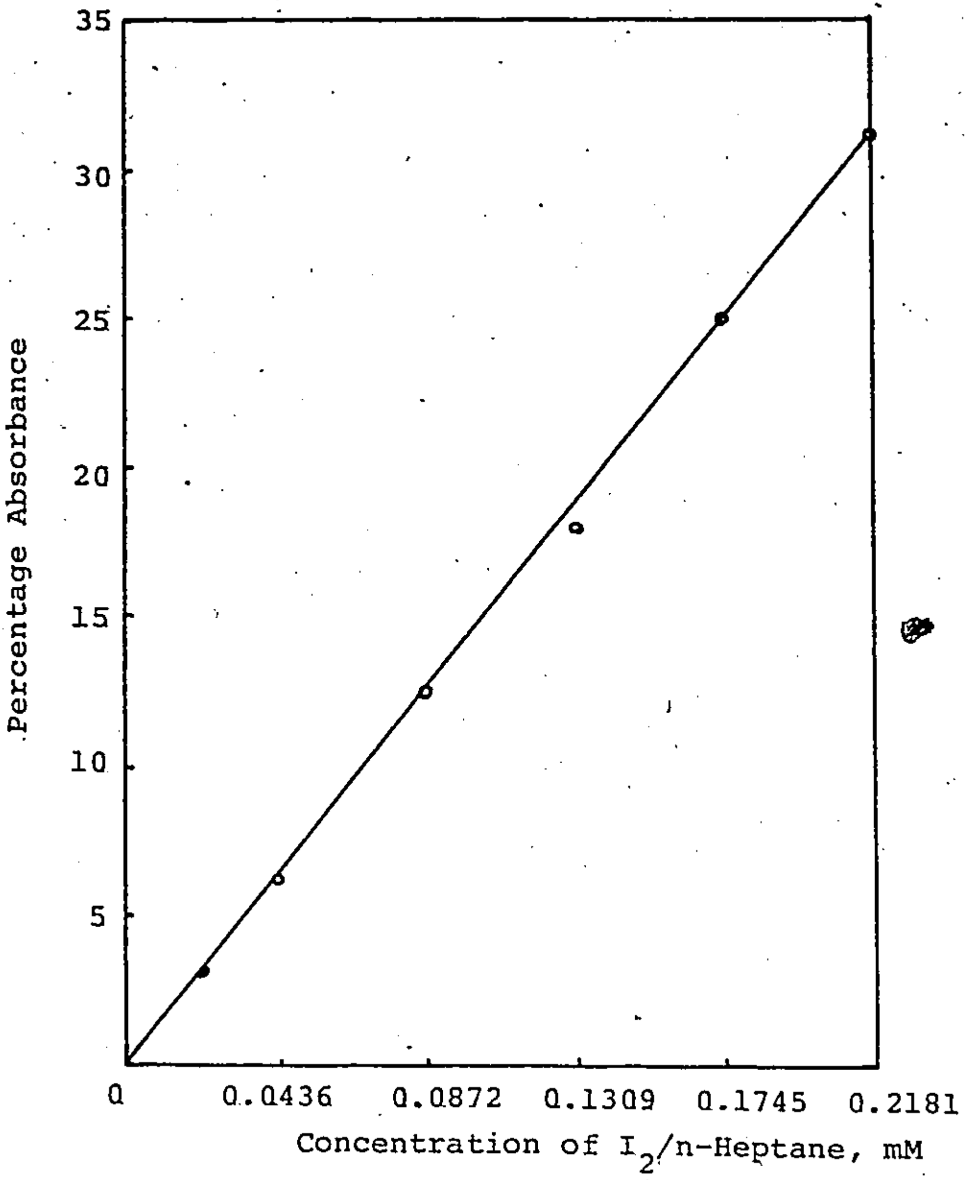


FIGURE 10 Photometer Calibration Curve for I_2/n-Heptane at 5250A°

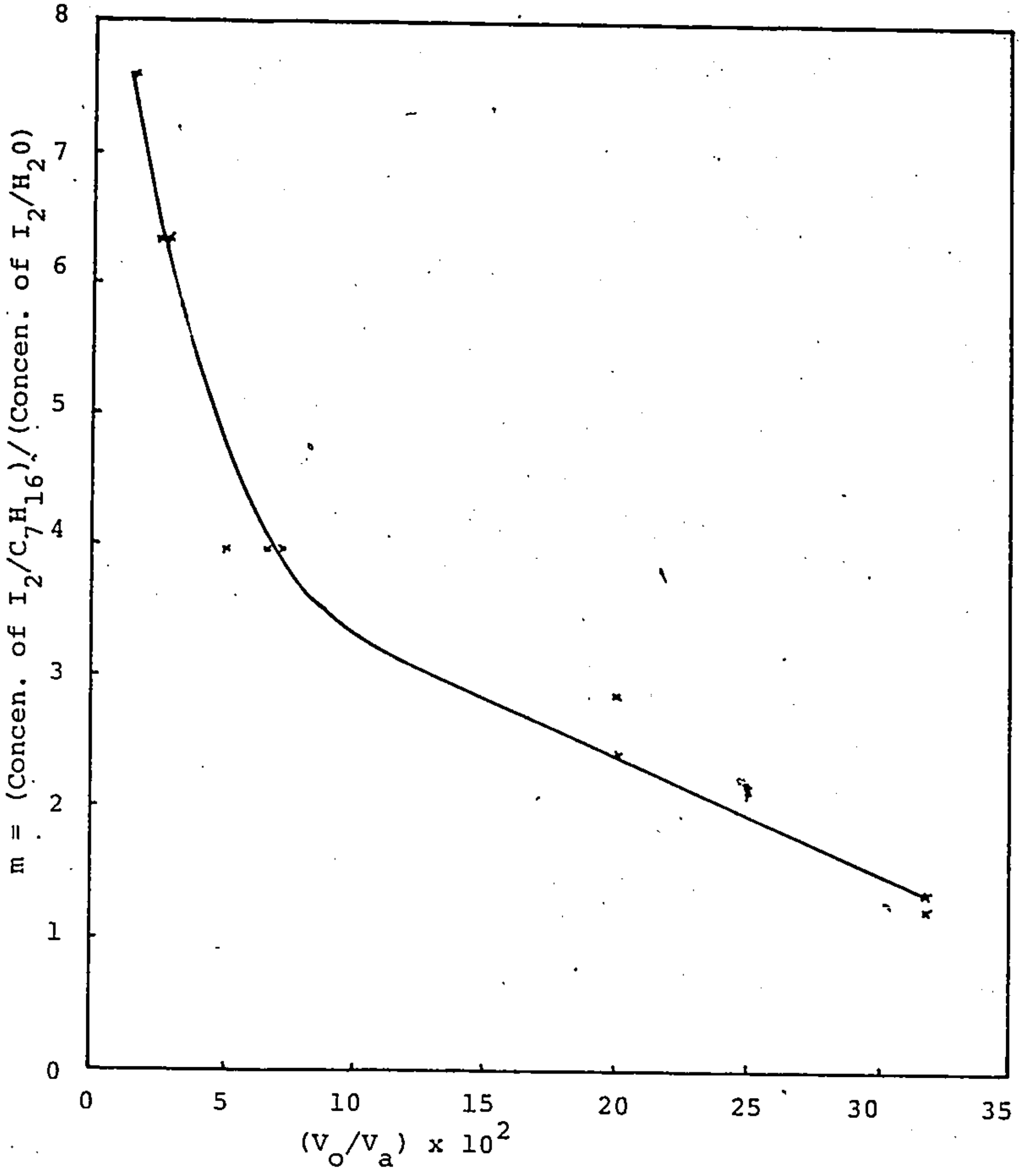


FIGURE 11 Distribution Constant vs. Phase Ratio for n-Heptane-Iodine/Water

for the distribution coefficient in all the calculations.

The experiment was carried out for three different slug lengths - 3,6, and 9 cm. - for different aqueous phase concentrations. Concentration of the slug with time for the three lengths is shown in Figs. 12,13 and 14 respectively. Also shown in the figures are curves for the same slug lengths but with the disc being used.

Calculation of mass transfer coefficients - K_a, k_o and k_a

The equilibrium curve between the two phases is assumed to be a straight line because of the reasons discussed above. The generalized diagram for the overall concentration differences is shown in Fig. 15 and let 'm' be the slope of the equilibrium line.

From Eqn. (9)

$$N_A = v_s \frac{dc_s}{dt} = K_a A_s (C_a - C_a^*)$$

But $$C_a^* = C_s/m$$

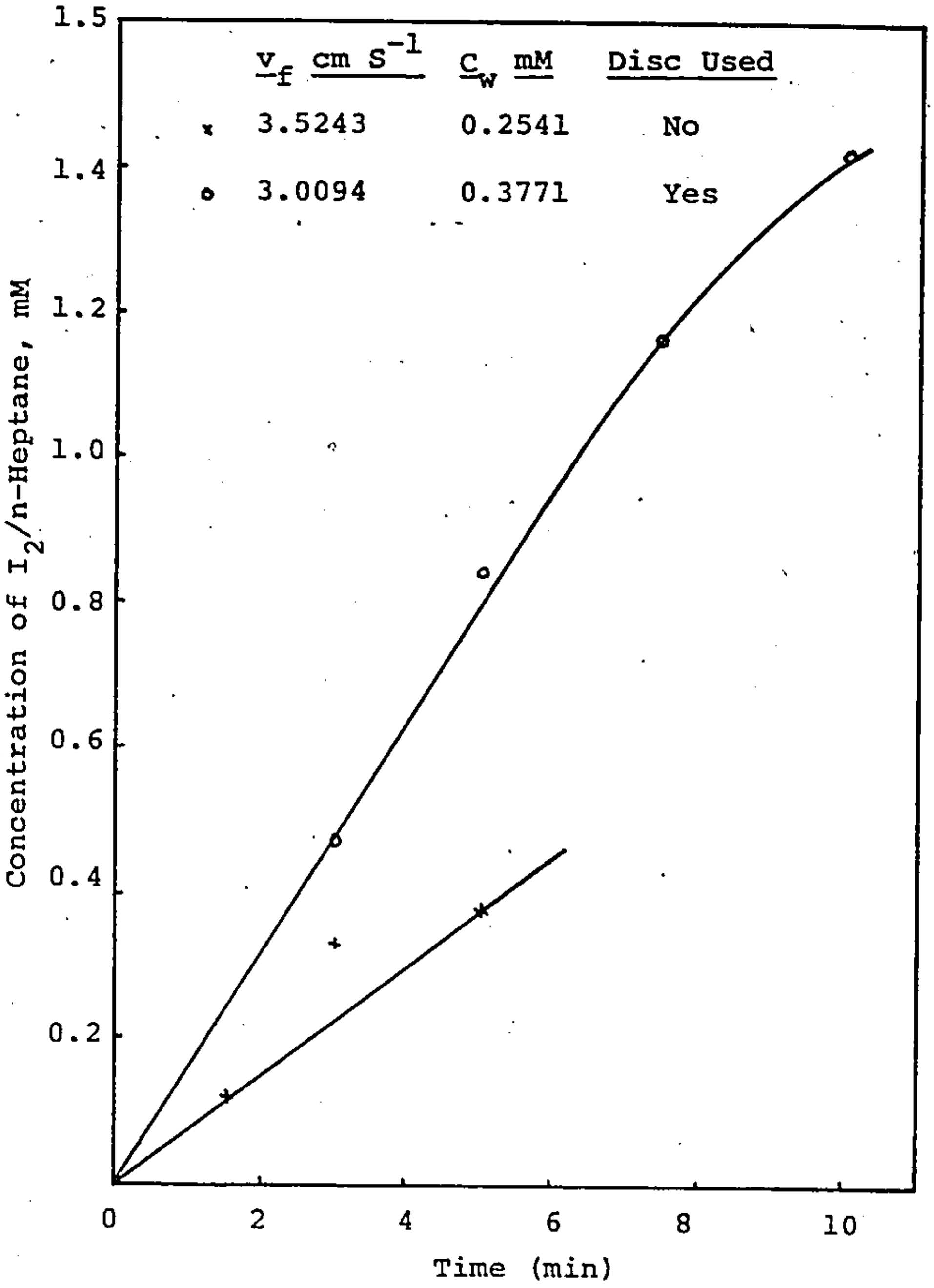
$$\therefore \quad v_s \frac{dc_s}{dt} = K_a A_s (C_a - C_s/m)$$

Rearranging and integrating the expression within the limits:

$$C_s = C_{s_1} \quad \text{at} \quad t = t_1$$

$$C_s = C_{s_2} \quad \text{at} \quad t = t_2$$

to obtain: $$K_a(t_2-t_1) = -\left(\frac{v_s m}{A_s}\right) \ln\left(\frac{C_a - C_{s_1}/m}{C_a - C_{s_2}/m}\right)$$



	v_f cm S^{-1}	C_w mM	Disc Used
×	3.5243	0.2541	No
o	3.0094	0.3771	Yes

FIGURE 12 Concentration vs Time for n-Heptane-Iodine/Water (L = 30 mm, Series 4)

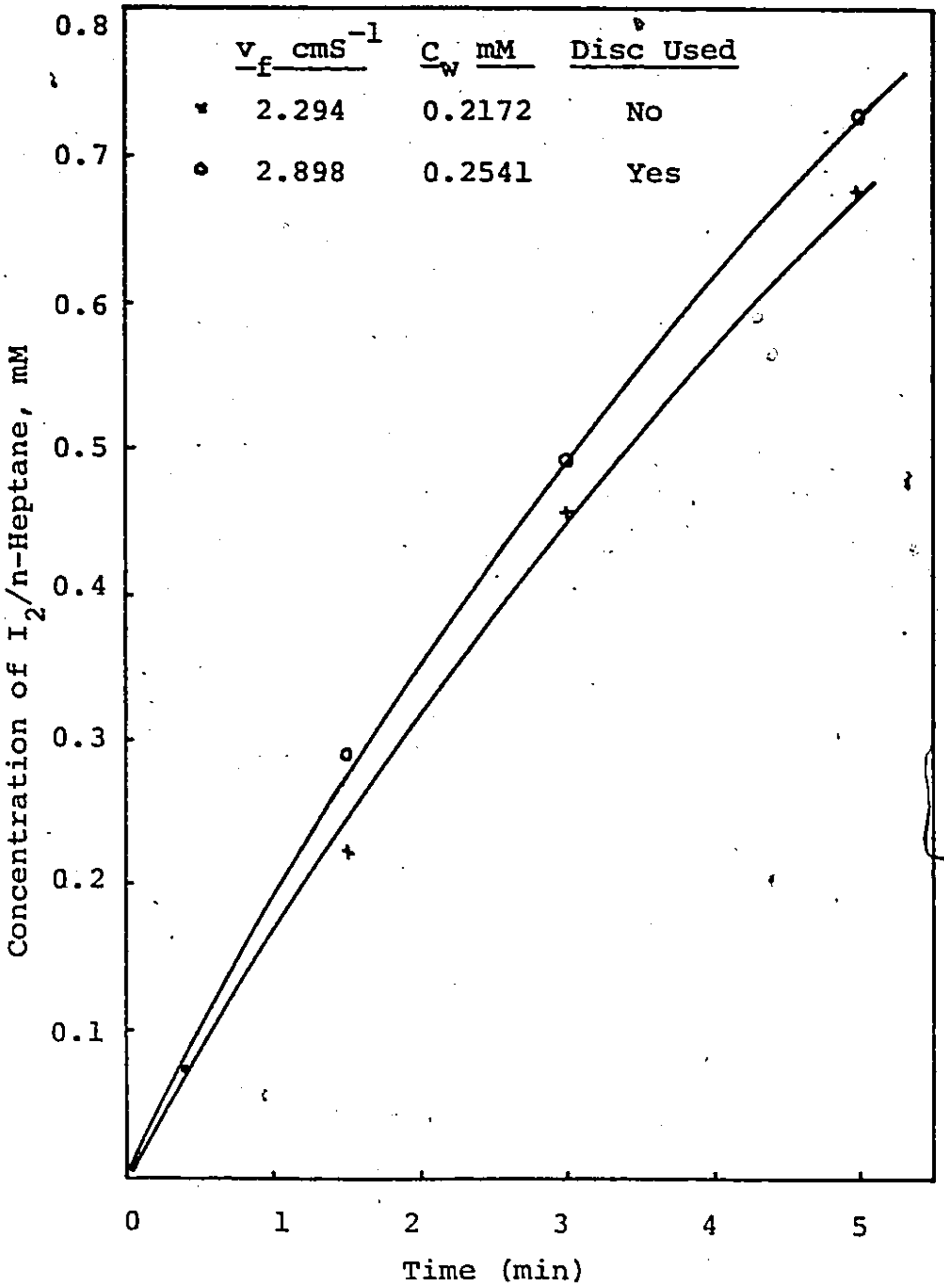


FIGURE 13 Concentration vs Time for n-Heptane-Iodine/Water (L = 60mm, Series 4)

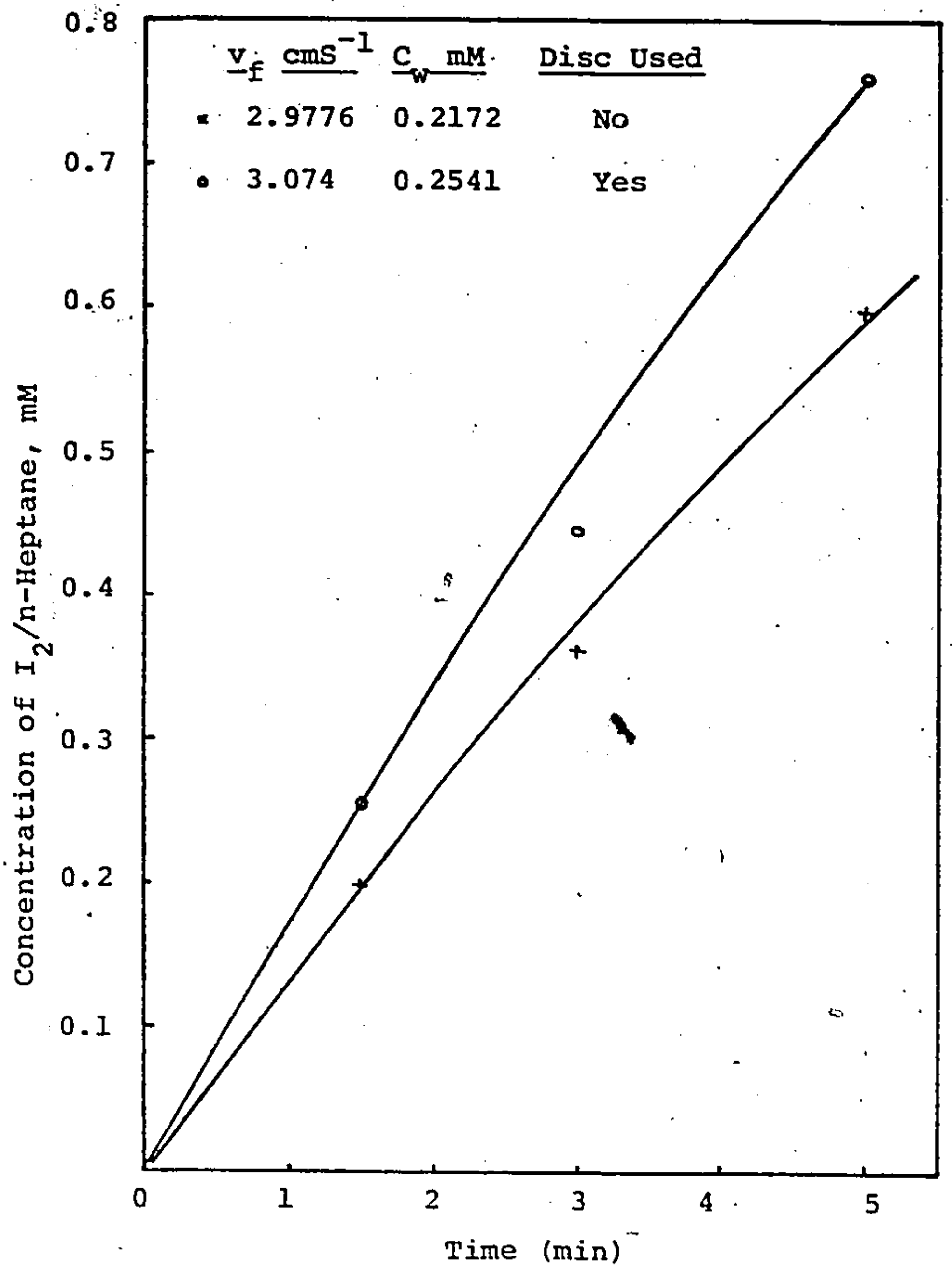


FIGURE 14 Concentration vs Time for n-Heptane-Iodine/Water (L = 90mm, Series 4)

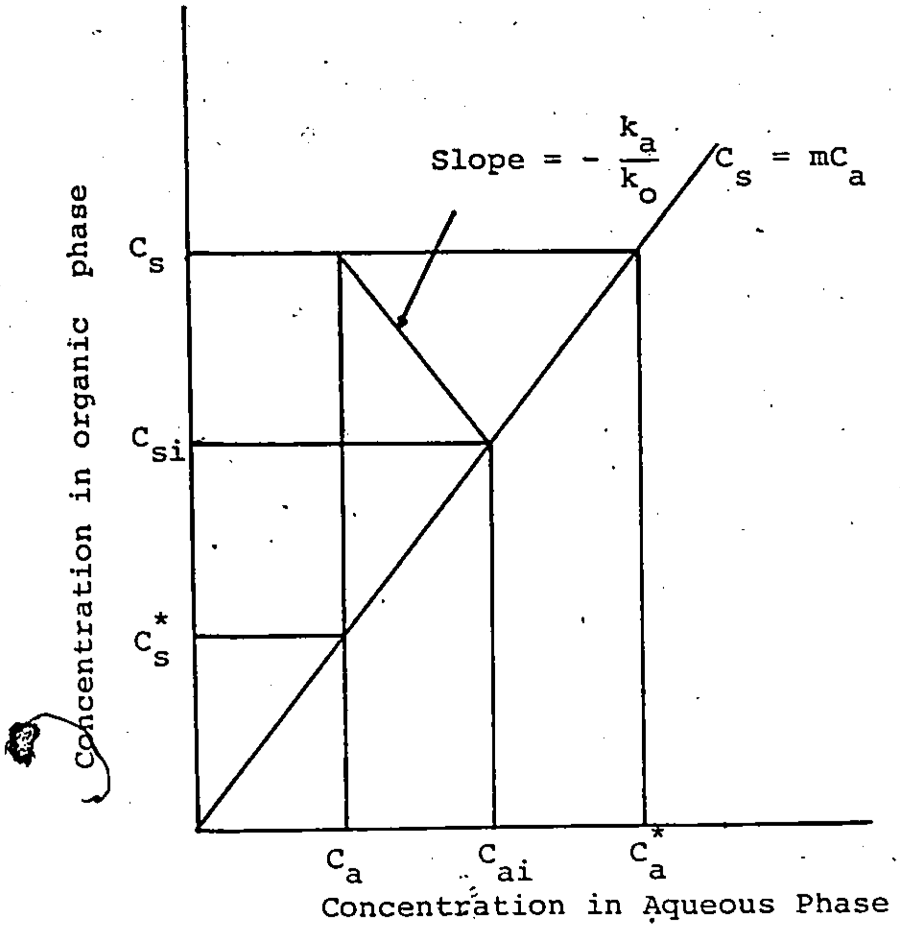


FIGURE 15 Generalized diagram for overall concentration differences

or $$K_a = -\frac{mv_s}{A_s(t_2-t_1)}\ln\left(\frac{1-x_1}{1-x_2}\right) \tag{19}$$

where $X = \frac{C_s}{mC_a}$

The experimental and predicted mass transfer coefficients are given in Tables 5-7 for the three slug lengths with other pertinent data. The individual phase coefficients are obtained in the following manner.

It was assumed that the mass transfer mechanism follows the Higbie's theory. Then:

$$\frac{k_a}{k_o} = \sqrt{\frac{D_a}{D_o}} = m' \text{ (say)} \tag{20}$$

where D_a and D_o are the respective diffusivities of the transferring solute at infinite dilution in the aqueous and organic phases.

But, from Eqn. (10),

$$\frac{1}{K_a} = \frac{1}{k_a} + \frac{1}{mk_o} \tag{21}$$

combining Eqns. (20) and (21) to get:

$$k_o = \frac{(m + m')}{mm'} K_a \tag{22a}$$

$$k_a = \frac{(m + m')}{m} K_a \tag{22b}$$

Eqns. (19) and (22) together give the individual phase coefficients.

MASS TRANSFER COEFFICIENTS - EXPERIMENT AND THEORY

TABLE 5 n-HEPTANE - IODINE/WATER - L = 30 mm

Interval (min)	Free Slug		Suspended Slug	
	$k_o x10^5$ m/s	$k_a x10^5$ m/s	$k_o x10^5$ m/s	$k_a x10^5$ m/s
0-1.5	2.8967	1.5439	4.328	2.258
1.5-3	2.889	1.540	5.7255	3.0517
3-5	3.005	1.602	4.4951	2.3954
5-7.5	-	-	4.058	2.1629
Penetration Theory	23.4	12.47	15.75	8.395

TABLE 6 n-HEPTANE - IODINE/WATER - L = 60 mm

Interval (min)	Free Slug		Suspended Slug	
	$k_o x10^5$ m/s	$k_a x10^5$ m/s	$k_o x10^5$ m/s	$k_a x10^5$ m/s
0-1.5	6.882	3.668	7.673	4.09
1.5-3	8.056	4.295	6.00	3.197
3-5	6.753	3.600	5.969	3.181
Penetration Theory	22.17	11.82	15.52	8.273

TABLE 7 n-HEPTANE - IODINE/WATER - L = 90 mm

Interval (min)	Free Slug		Suspended Slug	
	$k_o x 10^5$ m/s	$k_a x 10^5$ m/s	$k_o x 10^5$ m/s	$k_a x 10^5$ m/s
0-1.5	6.053	3.226	6.636	3.537
1.5-3	5.444	2.901	5.555	2.955
3-5	6.802	3.625	7.909	4.216
Penetration Theory	22.17	11.82	12.936	6.894

4.5 System: n-Heptane/Iodine - Sodium Thiosulphate/ Water

This is similar to the series 1 experiments except that now the solvent is n-Heptane. The initial concentrations in the slug and aqueous phases were 13.336 and 0.9827mM respectively.

The reaction is assumed to be instantaneous and takes place at the interface. The estimation of mass transfer coefficient is simple and follows the procedure given under series 1. Eqn. (16) is used to obtain k_o.

The experiment was carried out for a single slug length. Concentration of the slug (log) with time is shown in Fig. 16. The actual and predicted mass transfer coefficients are shown in Table 8. Concentration data are provided in Appendix A.

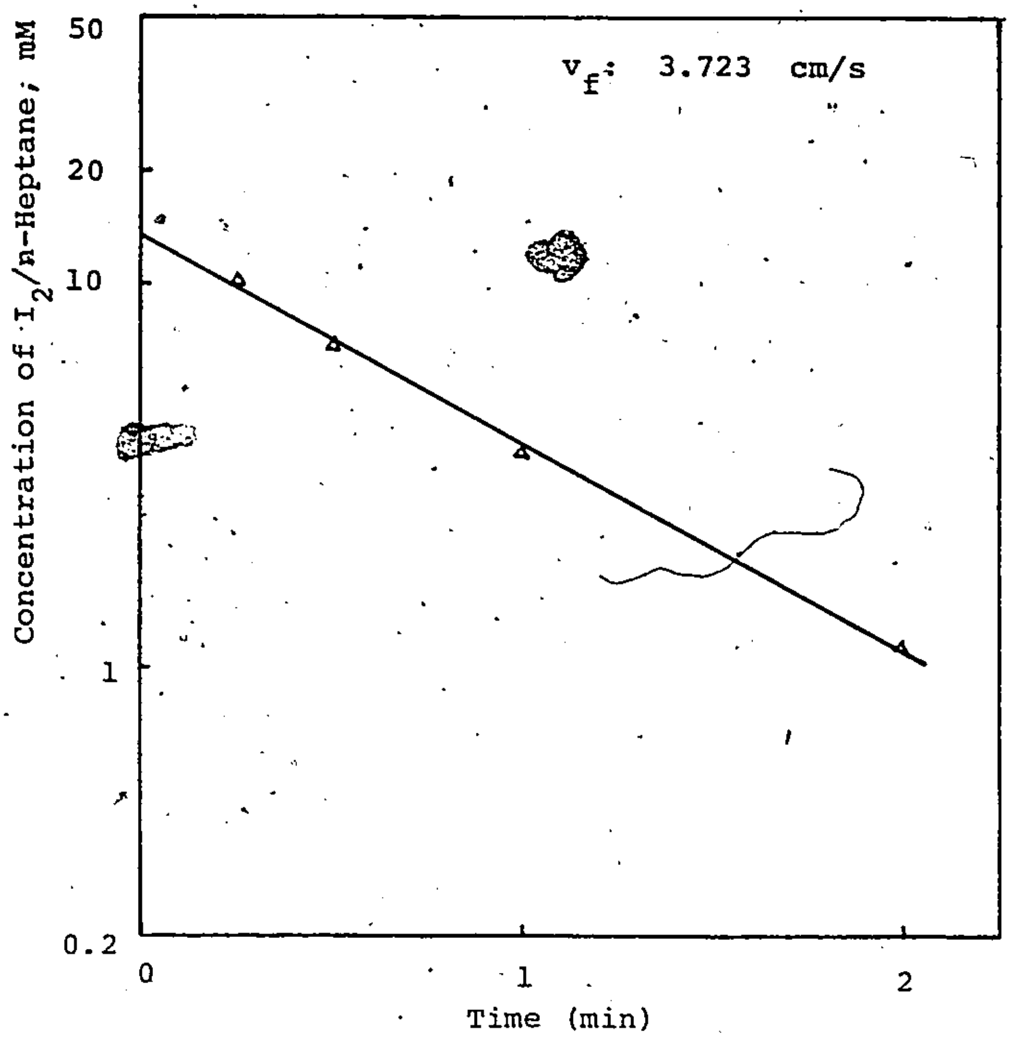


FIGURE 16 Concentration (log) vs Time for n-Heptane/I_2-$Na_2S_2O_3$/H_2O (Free slug)

TABLE 8 n-HEPTANE/IODINE - SODIUM THIOSULPHATE/WATER

Characteristic	Value
L	60 mm
v_f	0.3072 m/s
v_i	0.2932 m/s
ϕ	0.9214
k_o - Experiment	0.5897×10^{-4} m/s
k_o - Penetration Theory	1.326×10^{-4} m/s

CHAPTER 5

MASS TRANSFER EXPERIMENTS AND THE RESULTS WITH DISC-TYPE APPARATUS

It was mentioned in Chapters 3 and 4 that the free-slug apparatus has a serious disadvantage. For a given length of the same fluid, only single aqueous phase flow rate could be maintained which would keep the slug stationary. This problem was overcome in the disc-type apparatus and the experiments could be performed with different aqueous phase flow rates while other conditions remaining the same.

5.1 System: n-Heptane-Iodine/Water

This series of the experiments forms the main body of experiments. The transferring solute was iodine, initially present in the aqueous phase. Distribution data are given in Fig. 11 (Section 4.4). Experiments were performed for two variables of study - length of the slug and aqueous phase flow rate. The slug lengths studied were 3,6,9 and 12 cm. The range of v_f studied is 0.6389 to 3.074 cm/s. The concentration versus time data are shown in Figs. 17-20. The values of v_f and concentration of aqueous phase are indicated. The value of distribution coefficient used in the calculations was 9.412 corresponding to an organic/aqueous phase ratio approaching zero. The procedure of calculation of mass transfer coefficients follows that given in Section 4.4. Eqns. (19) and (22) together give the individual phase coefficients. These values are presented in Tables 9-24.

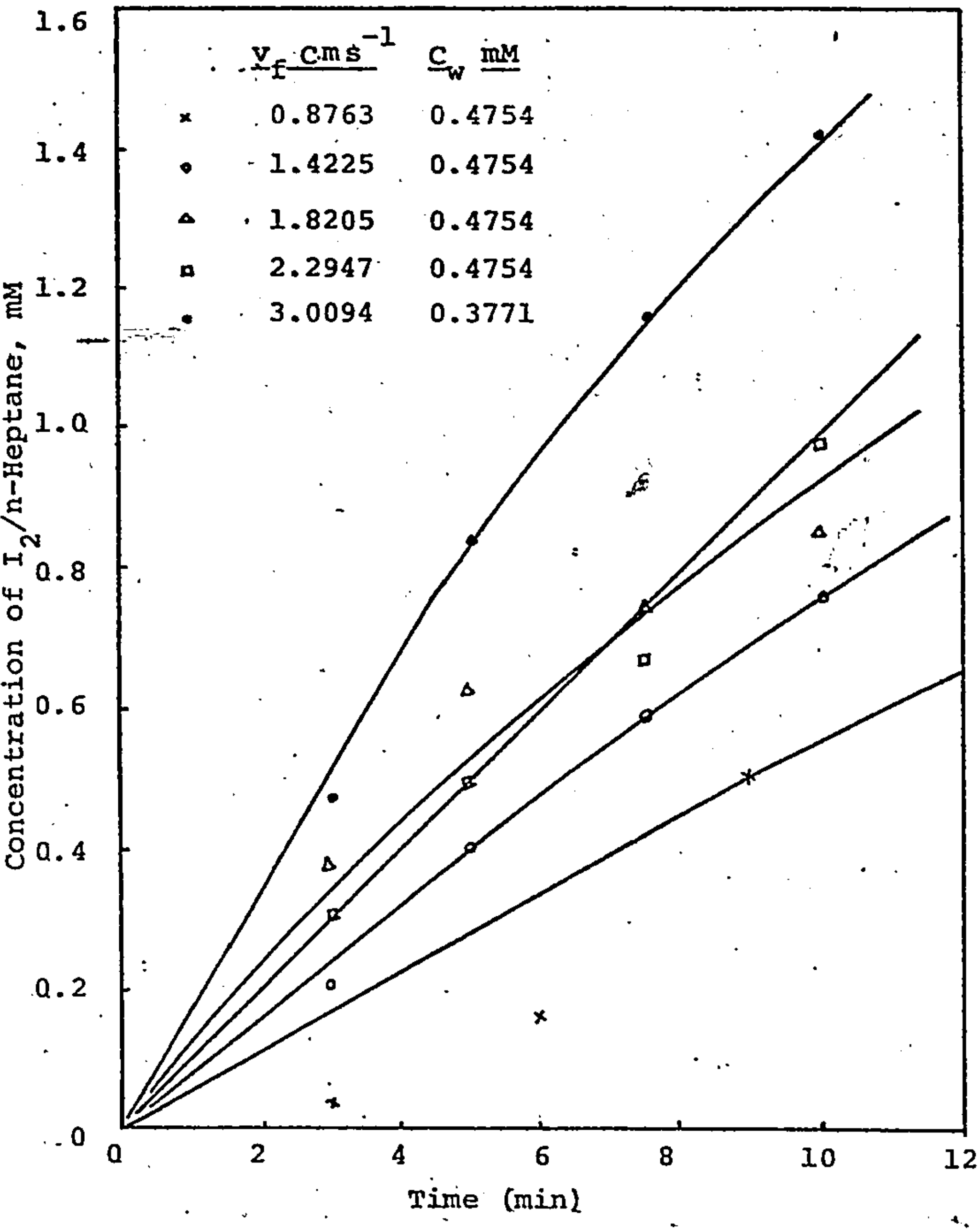


FIGURE 17 Concentration vs Time for n-Heptane-Iodine/Water (L = 30 mm, Series 6)

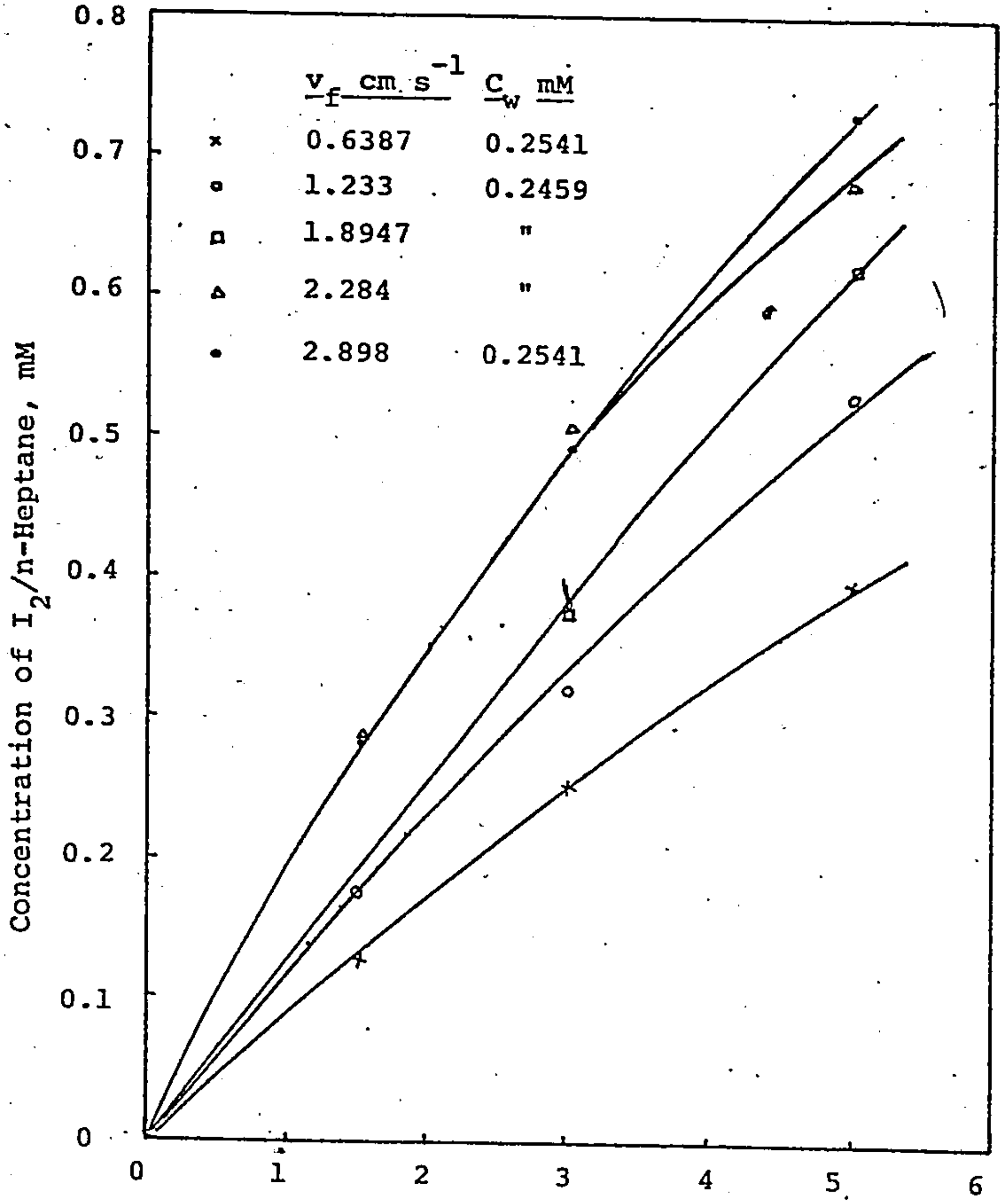


FIGURE 18 Concentration vs Time for n-Heptane-Iodine/Water (L = 60 mm, Series 6)

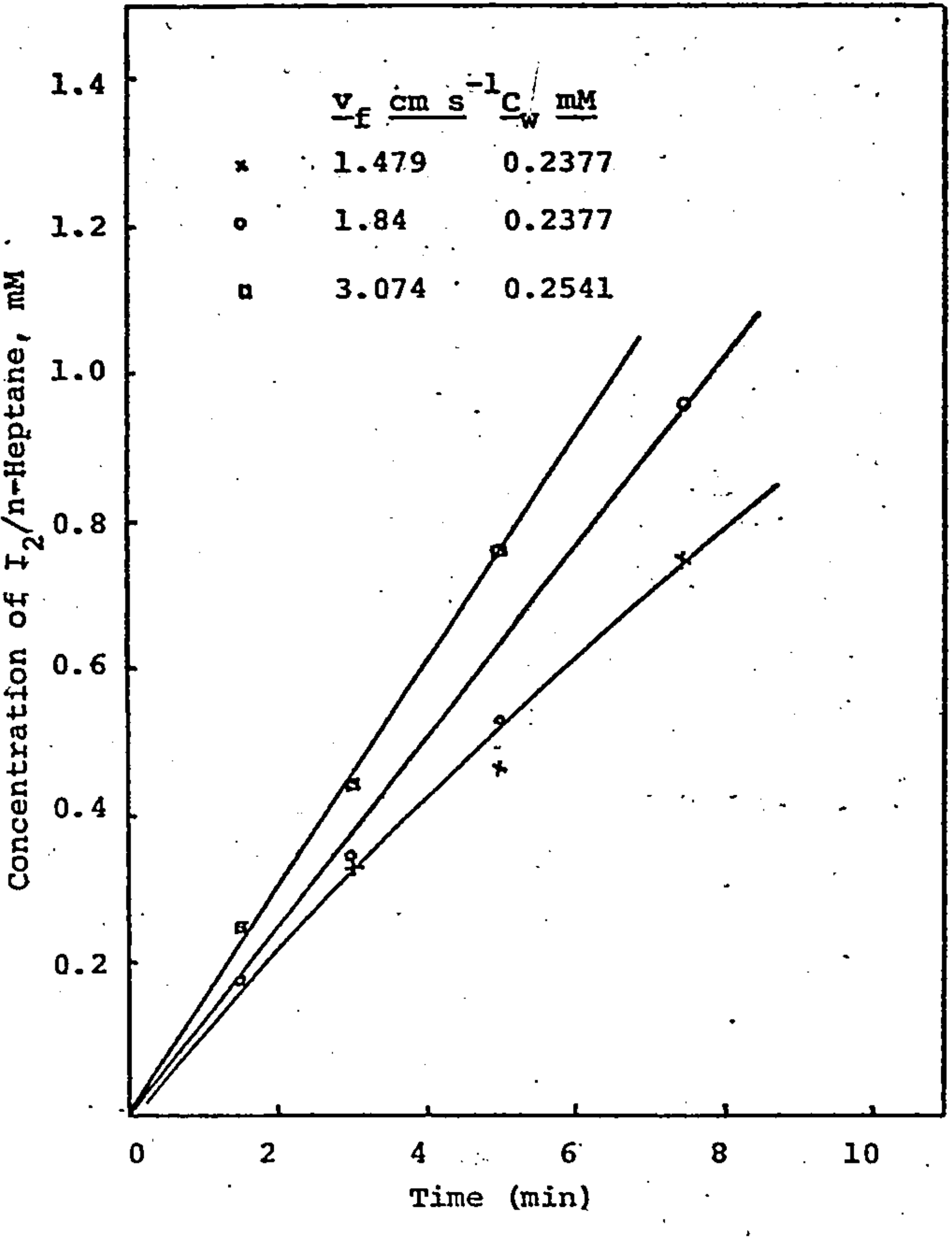


FIGURE 19 Concentration vs Time for n-Heptane-Iodine/Water (L = 90 mm, Series 6)

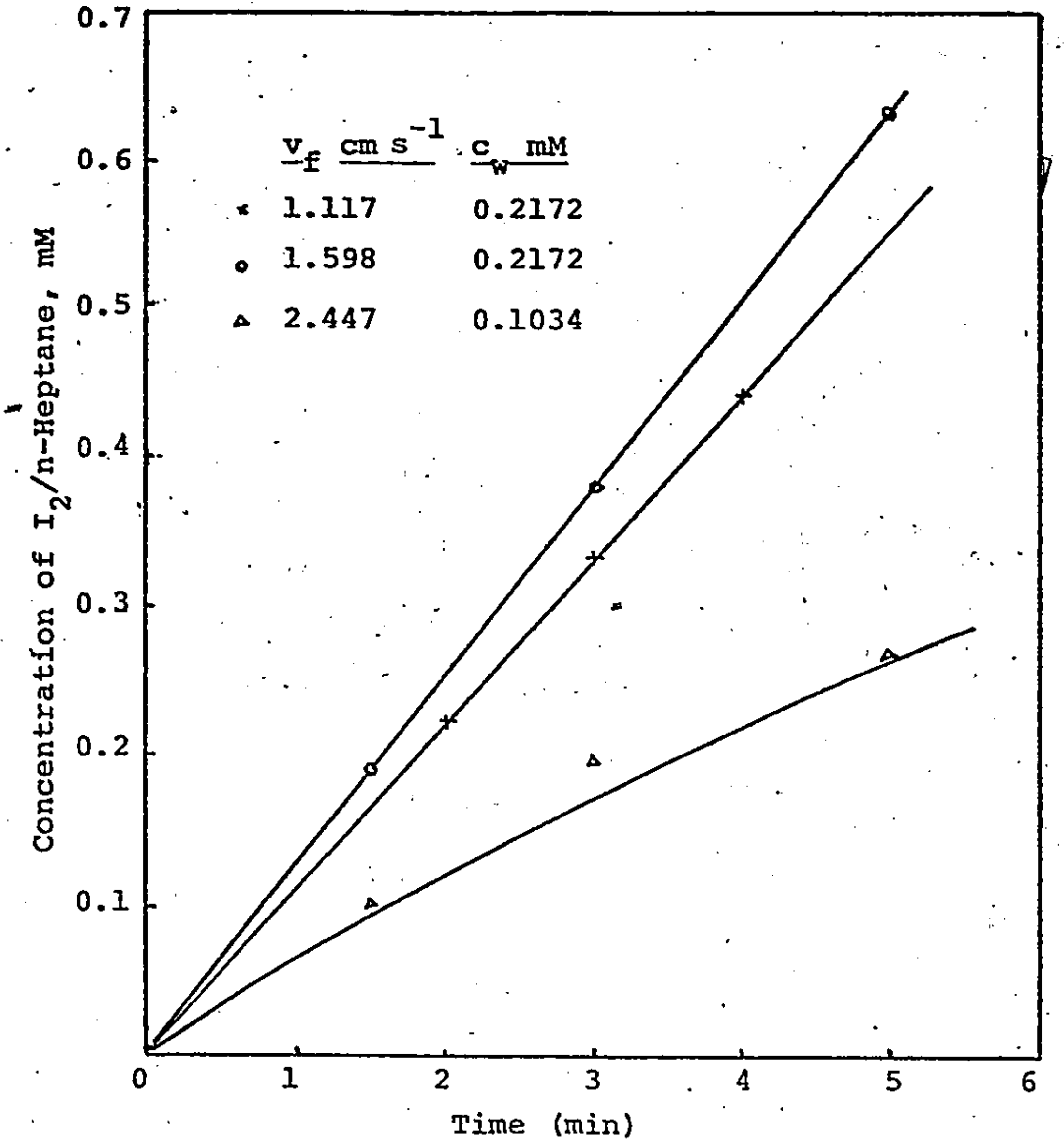


FIGURE 20 Concentration vs Time for n-Heptane-Iodine/Water (L = 120 mm, Series 6).

MASS TRANSFER COEFFICIENTS - EXPERIMENT AND THEORY (SERIES 6)

TABLE 9 FOR L = 30 mm, v_f = 0.0088 m/s
(v_i: 0.1328 m/s, ϕ: 0.9504)

Interval (min)	$k_o \times 10^5$ m/s	$k_a \times 10^5$ m/s
0-3	0.252	0.1343
3-6	0.8635	0.4603
6-9	2.5362	1.352
9-12	1.1521	0.6141
Penetration Theory:	14.83	7.91

TABLE 10 FOR L = 30 mm. v_f = 0.0142 m/s
(v_i: 0.183 m/s; ϕ: 0.9412)

Interval (min)	$k_o \times 10^5$ m/s	$k_a \times 10^5$ m/s
0-3	1.4301	0.7622
3-5	2.1464	1.144
5-7.5	1.7142	0.9136
7.5-10	1.6234	0.8652
Penetration Theory:	17.41	9.28

TABLE 11 FOR L = 30 mm, v_f = 0.0182 m/s

(v_i: 0.2157 m/s, ϕ:0.9358)

Interval (min)	$k_o \times 10^5$ m/s	$k_a \times 10^5$ m/s
0-3	2.7629	1.4247
3-5	2.7643	1.4734
5-7.5	1.1348	0.6048
7.5-10	1.0822	0.5768
Penetration Theory:	18.9	10.08

TABLE 12 FOR L = 30 mm, v_f = 0.0229 m/s

(v_i: 0.2505 m/s, ϕ: 0.9304)

Interval (min)	$k_o \times 10^5$ m/s	$k_a \times 10^5$ m/s
0-3	1.7674	0.942
3-5	2.61	1.391
5-7.5	1.6073	0.8567
7.5-10	3.0684	1.636
Penetration Theory:	20.37	10.86

TABLE 13 FOR L = 30 mm, v_f = 0.03 m/s

(v_i: 0.2995 m/s, ϕ: 0.9232)

Interval (min)	$k_o x10^5$ m/s	$k_a x10^5$ m/s
0-3	4.328	2.258
3-5	5.7255	3.0517
5-7.5	4.4951	2.3959
7.5-10	4.058	2.1629
Penetration Theory:	22.28	11.87

TABLE 14 FOR L = 60 mm, v_f = 0.0064 m/s

(v_i: o.1081 m/s, ϕ: 0.9552)

Interval (min)	$k_o x10^5$ m/s	$k_a x10^5$ m/s
0-1.5	3.388	1.806
1.5-3	3.428	1.827
3-5	3.227	1.72
Penetration Theory:	9.46	5.043

TABLE 15 FOR L = 60 mm, v_f = 0.0123 m/s
(v_i: 0.1672 m.s, ϕ: 0.944)

Interval (min)	$k_o x10^5$ m/s	$k_a x10^5$ m/s
0-1.5	4.201	2.239
1.5-3	4.804	2.561
3-5	5.037	2.685
5-7.5	10.737	5.723
Penetration Theory:	11.765	6.272

TABLE 16 FOR L = 60 mm, v_f = 0.0189 m/s
(v_i: 0.2209 m/s, ϕ: 0.935)

Interval (min)	$k_o x10^5$ m/s	$k_a x10^5$ m/s
0-1.5	4.759	2.536
1.5-3	5.846	3.116
3-5	6.102	3.253
5-7.5	11.485	6.121
Penetration Theory:	13.52	7.21

TABLE 17 FOR L = 60 mm, v_f = 0.0228 m/s

(v_i: 0.2494 m/s, ϕ: 0.9306)

Interval (min)	$k_o x10^5$ m/s	$k_a x10^5$ m/s
0-1.5	7.898	4.21
1.5-3	6.874	3.664
3-5	4.496	2.396
Penetration Theory:	14.37	7.66

TABLE 18 FOR L = 60 mm, v_f = 0.02898 m/s

(v_i: 0.2908 m/s, ϕ: 0.924)

Interval (min)	$k_o x10^5$ m/s	$k_a x10^5$ m/s
0-1.5	7.673	4.09
1.5-3	6.00	3.197
3-5	5.969	3.189
Penetration Theory:	15.52	8.273

TABLE 19 FOR L = 90 mm, v_f = 0.0148 m/s
(v_i: 0.1271 m/s, ϕ: 0.9402)

Interval (min)	$k_o \times 10^5$ m/s	$k_a \times 10^5$ m/s
0-1.5	5.1728	2.757
1.5-3	4.403	2.347
3-5	3.332	1.776
5-7.5	6.331	3.375
Penetration Theory:	8.378	4.466

TABLE 20 FOR L = 90 mm, v_f = 0.0184 m/s
(v_i: 0.2169 m/s, ϕ: 0.9354)

Interval (min)	$k_o \times 10^5$ m/s	$k_a \times 10^5$ m/s
0-1.5	4.93	2.628
1.5-3	5.192	2.767
3-5	4.462	2.378
5-7.5	10.582	5.64
Penetration Theory:	10.945	5.834

TABLE 21 FOR L = 90 mm, v_f = 0.0307 m/s

(v_i: 0.303 m/s, ϕ: 0.9226)

Interval (min)	$k_o x10^5$ m/s	$k_a x10^5$ m/s
0-1.5	6.636	3.537
1.5-3	5.555	2.955
3-5	7.909	4.216
Penetration Theory:	12.936	6.894

TABLE 22 FOR L = 120 mm, v_f = 0.0112 m/s*

(v_i: 0.156 m/s, ϕ: 0.9458)

Interval (min)	$k_o x10^5$ m/s	$k_a x10^5$ m/s
0-2	5.287	2.818
2-3	5.593	2.981
3-4	6.156	3.281
Penetration Theory:	8.039	4.285

---

*Turbulence was observed.

TABLE 23 FOR L = 120 mm, v_f = 0.016 m/s*

(v_i: 0.1972 m/s, ϕ: 0.9386)

Interval (min)	$k_o \times 10^5$ m/s	$k_a \times 10^5$ m/s
0-1.5	5.939	3.166
1.5-3	5.017	2.674
3-5	8.19	4.365
Penetration Theory:	9.027	4.817

TABLE 24 FOR L = 120 mm, v_f = 0.0245 m/s*

(v_i: 0.2615 m/s, ϕ: 0.9294)

Interval (min)	$k_o \times 10^5$ m/s	$k_a \times 10^5$ m/s
0-1.5	6.538	3.485
1.5-3	7.055	3.76
3-5	4.226	2.252
Penetration Theory:	10.407	5.547

---

*Turbulence was observed.

5.2 System: n-Heptane/Iodine-Water

This series of experiments consists of transfer of solute in the reverse of the earlier series, i.e., the solute transfers from organic to aqueous phase. Transferring solute was again iodine dissolved initially in n-Heptane.

The experiment was carried out for a single slug length of 6 cm and aqueous phase velocities from 1.09 to 2.87 cm/s. Concentration - time data are given in Appendix A and the mass transfer coefficients are given in Tables 25-28. Method of estimation of the coefficients is given below.

Estimation of mass transfer coefficients

The equilibrium curve between the two phases is assumed to be a straight line of slope m. The generalized diagram for the overall concentration differences is shown in Fig. 15.

From Eqn. (11)

$$N_A = -v_s \frac{dc_s}{dt} = K_o A_s (C_s - C_s^*) \tag{23}$$

but

$$C_s^* = mC_{av} = m\,C_{ae}/2 \tag{24}$$

where C_{av} = Average concentration in the aqueous phase film

C_{ae} = Concentration in the effluent stream

By material balance,

Moles of solute lost by the organic phase

= Moles gained by the aqueous phase.

$$\text{i.e.} \quad -v_s \frac{dc_s}{dt} = v_f A_t C_{ae} \qquad (25)$$

Eliminating C_s^* from Eqn. (23) using Eqns. (24) and (25) to get

$$-v_s\left(1 + \frac{mA_sK_o}{2v_fA_t}\right)\frac{dc_s}{dt} = K_oA_sC_s$$

Integrating the above equation within the limits

$$C_s = C_{s_1} \quad \text{at} \quad t = t_1$$

$$C_s = C_{s_2} \quad \text{at} \quad t = t_2$$

to obtain

$$v_s\left(1 + \frac{mA_sK_o}{2v_fA_t}\right)\ln\left(\frac{C_{s_1}}{C_{s_2}}\right) = K_oA_s(t_2 - t_1) \quad (26)$$

The value of K_o can be obtained from the slope of the line obtained by plotting $\ln(C_s/C_{so})$ vs time. The value of K_a can be obtained by multiplying K_o with m. Individual phase coefficients are calculated using Eqn. (22). Concentration (log) versus time curves are shown in Fig. 21.

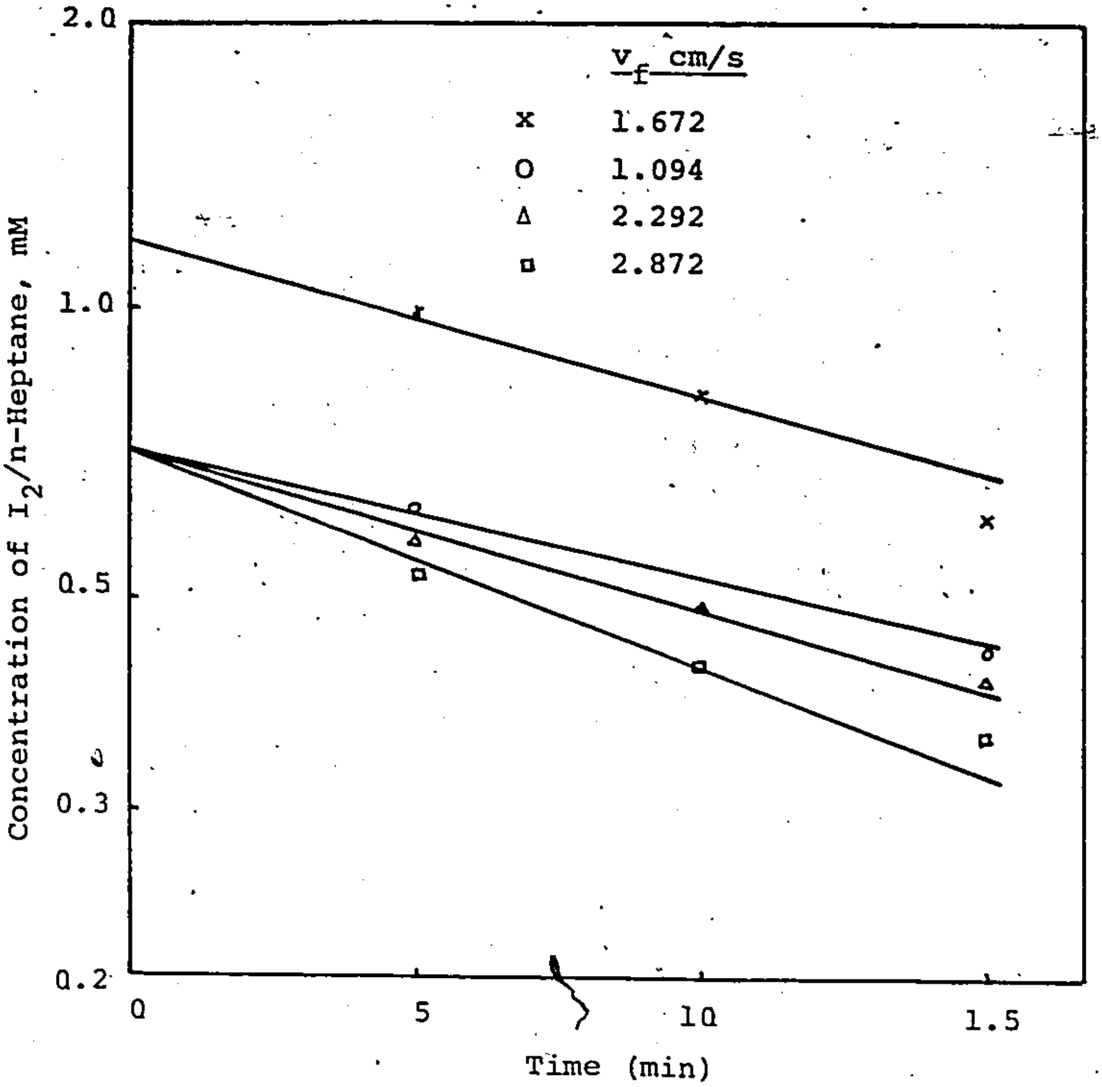


FIGURE 21 Concentration (log) vs. Time for n-Heptane/Iodine-Water

MASS TRANSFER COEFFICIENTS - EXPERIMENT AND THEORY (Series 7)

TABLE 25 FOR L = 60 mm, v_f = 0.0109 m/s/
(v_i: o.1535 m/s, ϕ: 0.9462)

Interval (min)	k_ox10^5 m/s	k_ax10^5 m/s
0-5	2.357	1.256
5-10	3.124	1.665
10-15	3.355	1.788
Penetration Theory:	11.276	6.01

TABLE 26 FOR L = 60 mm, v_f = 0.0167 m/s
(v_i: o.2032 m/s, ϕ: 0.9186)

Interval (min)	k_ox10^5 m/s	k_ax10^5 m/s
0-5	3.1084	1.6568
5-10	3.524	1.878
10-15	5.313	2.832
Penetration Theory:	12.974	6.915

TABLE 27 FOR L = 60 mm, v_f = 0.0229 m/s
v_i: 0.2499 m/s, ϕ: 0.9302)

Interval (min)	k_ox10^5 m/s	k_ax10^5 m/s
0-5	3.923	2.091
5-10	2.863	1.526
10-15	3.245	1.730
Penetration Theory:	14.388	7.699

TABLE 28 FOR L = 60 mm, v_f = 0.0287 m/s
(v_i: 0.2894 m/s, ϕ: 0.9134)

Interval (min)	k_ox10^5 m/s	k_ax10^5 m/s
0-5	5.409	2.878
5-10	3.838	2.046
10-15	2.995	1.596
Penetration Theory:	15.483	8.253

5.3 System: Iodine/n-Heptane-Sodium Thiosulphate/Water

The transferring solute was iodine from n-Heptane and was reacting with sodium thiosulphate in the aqueous phase. It was assumed that the reaction is instantaneous and takes place at the interface.

The experiment was carried out for a slug length 6 cm and aqueous phase flow rate of 3.206 cm/s. This flow rate was chosen because it is nearly close to the aqueous phase flow rate which had to be maintained to keep 6 cm long slug stationary in the free-slug apparatus. Thus the mass transfer rates in the two cases could be compared. Concentration time data are shown in Fig. 22 (semi-log) and tabulated in Appendix A for both cases. The data for free slug are taken from Section 4.5.

Mass transfer coefficients - experiment and predicted are shown in Table 29. Also given in table are those corresponding to the free slug experiment. Calculation of the coefficients is based on Eqn. (16) given in Section 4.1.

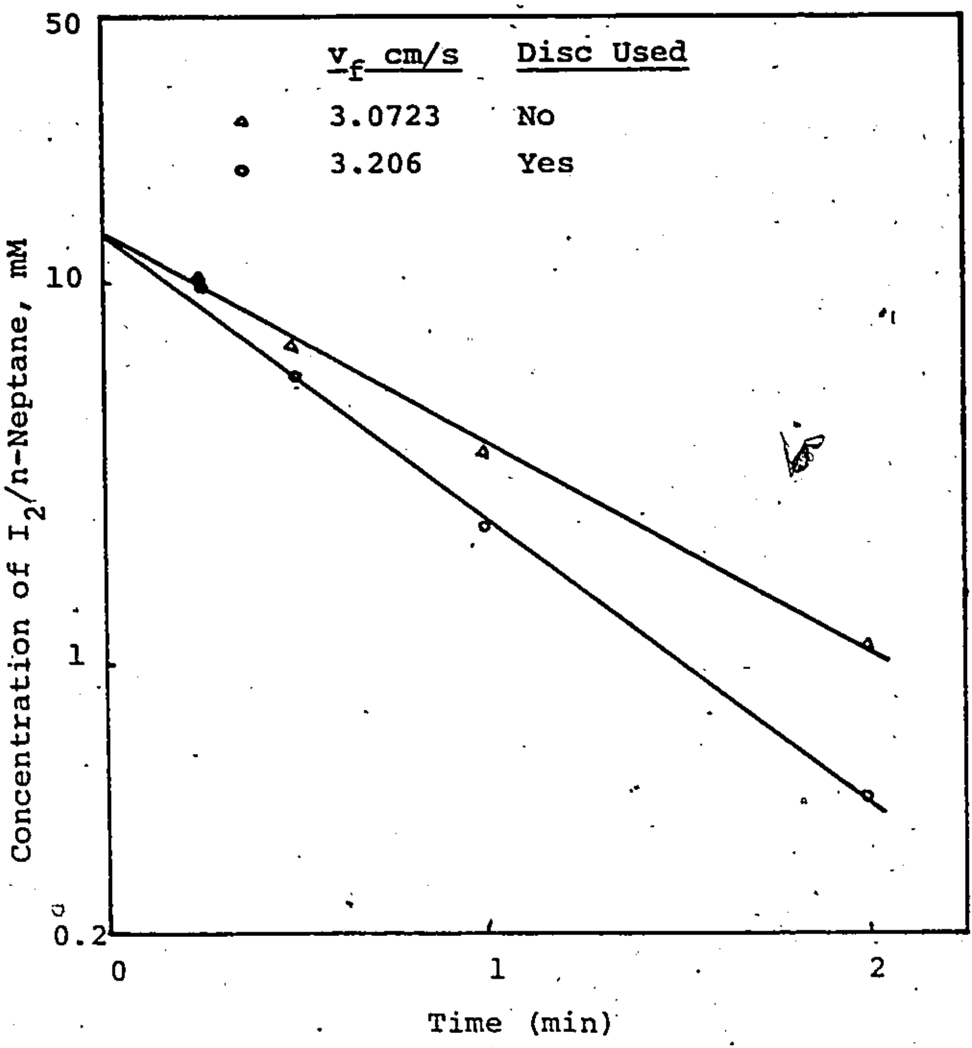


FIGURE 22 Concentration (log) vs time for n-Heptane/I_2 - $Na_2S_2O_3/H_2O$

TABLE 29 MASS TRANSFER COEFFICIENTS - FREE AND SUSPENDED SLUGS
(L = 60 mm, Series 8)

Characteristic	Suspended-Slug	Free-Slug
v_f	0.0321 m/s	0.0307 m/s
v_i	0.3021 m/s	0.2932
ϕ	0.9201	0.9214
k_o -		
Experiment	0.8047×10^{-4} m/s	0.5897×10^{-4} m/s
Penetration Theory	1.3462×10^{-4} m/s	1.326×10^{-4} m/s

5.4 System: n Heptane/Acetic Acid-Water

In this last series, the transferring solute was acetic acid which is highly soluble in the aqueous phase. Acetic acid was initially dissolved in the solvent, n-Heptane.

Distribution data for the system were obtained at various concentrations is the organic phase and the data are shown in Fig. 23. The resulting curve is highly non-linear. However, distribution coefficient was greater than at least thirty, in favour of the aqueous phase.

Experiment was performed for a single slug length and a single aqueous phase flow rate. The concentration-time (Semilog) data are shown in Fig. 24. Estimation of the mass transfer coefficient is based on Eqn. (16) and is given in Table 30 with other pertinent data. Concentration-time data are also given in Appendix A.

TABLE 30 MASS TRANSFER COEFFICIENTS - EXPERIMENT AND PREDICTED (Series 9)

Characteristic	Value
L	60 mm
v_f	0.0136 m/s
v_i	0.174 m/s
ϕ	0.9410
k_o - Experiment	
Initial Drop	7.282×10^{-5} m/s
Straight Line Drop	0.2758×10^{-5} m/s
k_o - Penetration Theory	1.058×10^{-5} m/s

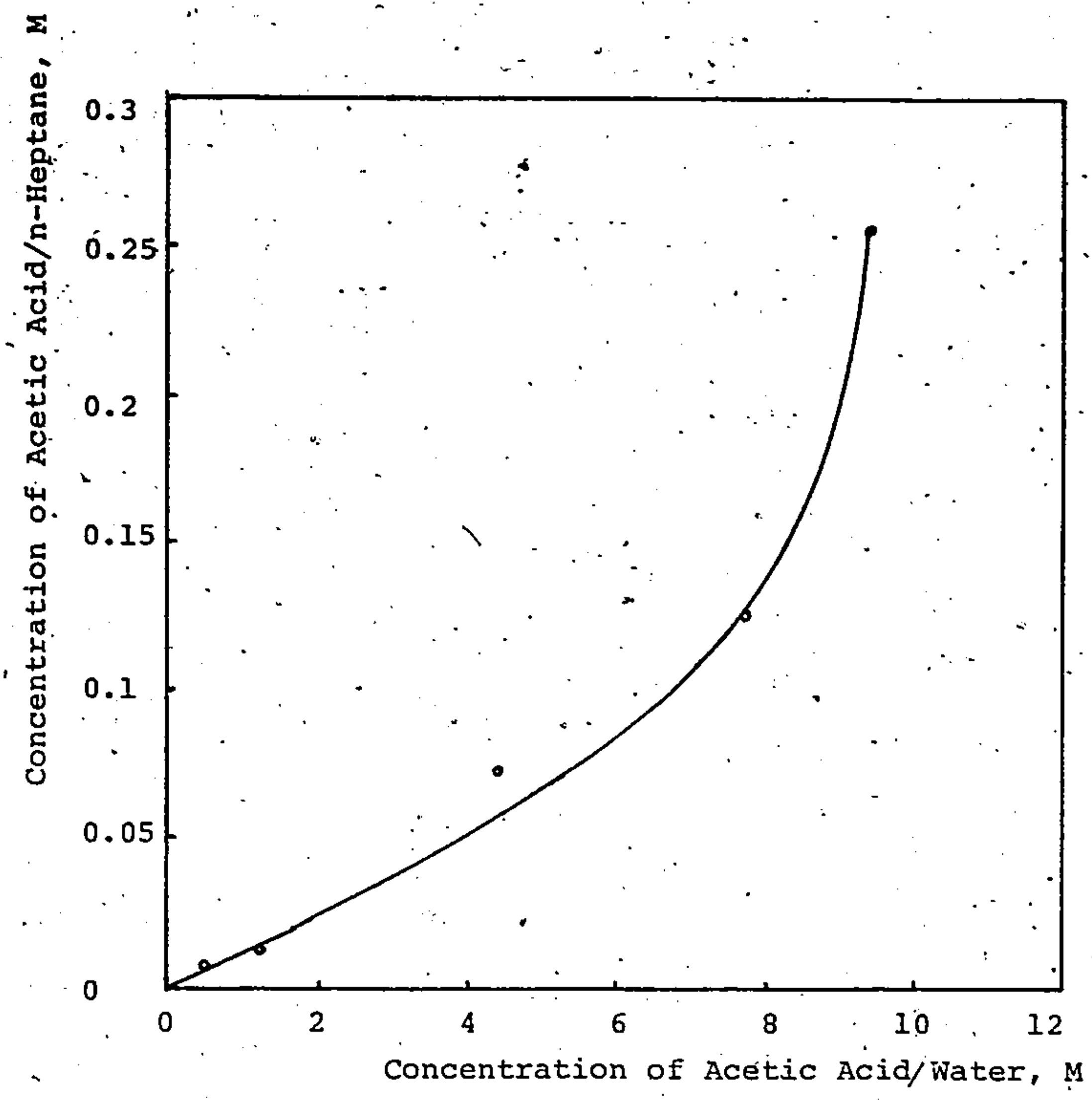


FIGURE 23 Concentration of Acetic Acid/n-Heptane vs Concentration of Acetic Acid/Water

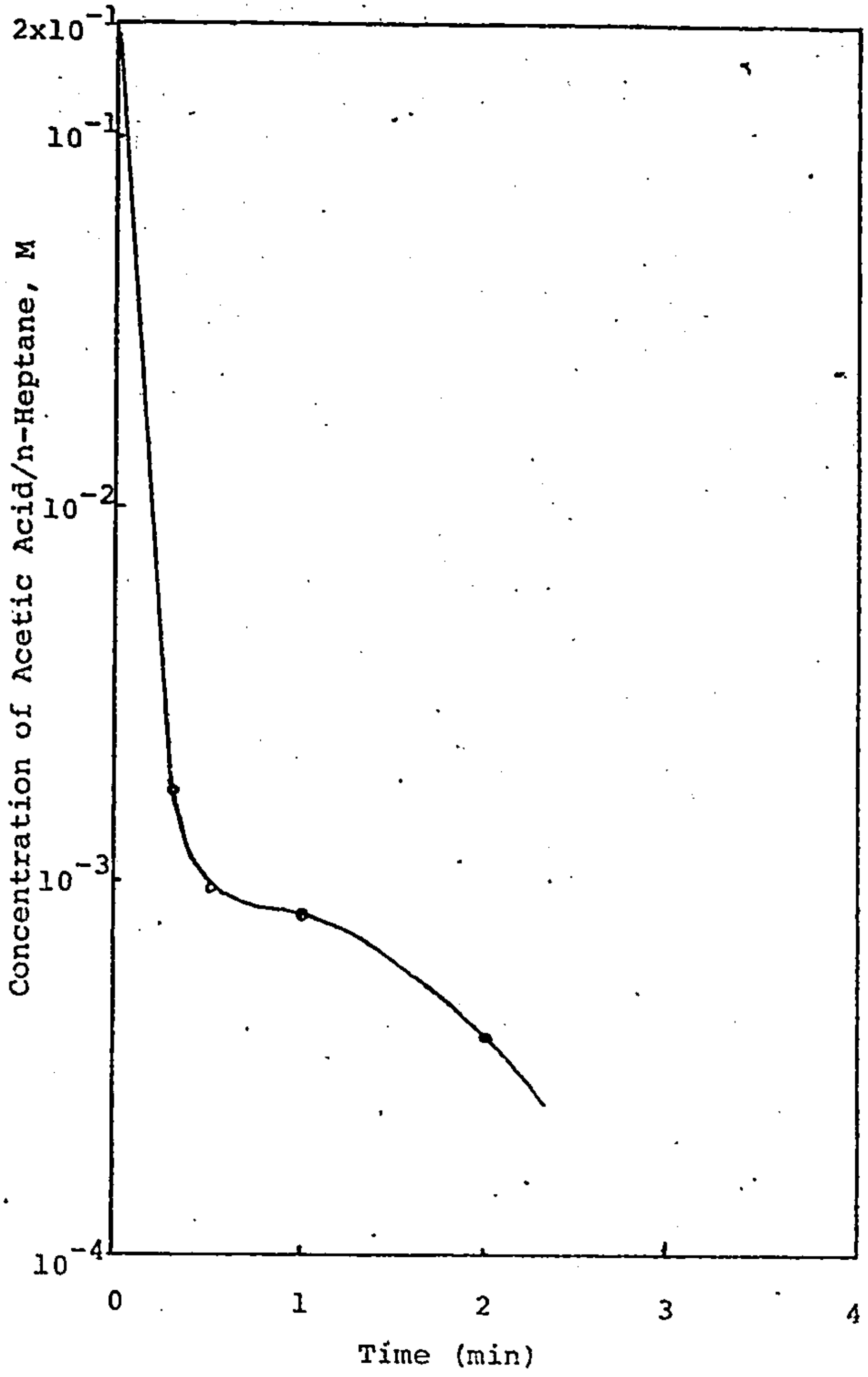


FIGURE 24 Concentration (log) vs time for n-Heptane/Acetic Acid-Water

CHAPTER 6

INTERFACIAL TENSION MEASUREMENTS DURING MASS TRANSFER

It is important in any ternary mass transfer to know whether surface forces are playing a part in the mass transfer. Because of this, measurement of interfacial tension (σ_i) was undertaken. Fisher Autotensiomat was the equipment used for measurements.

The system chosen was n-Heptane-Iodine-Water. In the first experiment, iodine was transferring from water to n-Heptane. Measurements were made at arbitrary times. The interfacial tension is plotted against time (Semi-log scale) in Fig. 25. In the second experiment, the solute was diffusing from the organic phase to the aqueous phase. The recorded values against time are shown in Fig. 26. In both experiments, duration of the experiment was 49 mins. The experiments were performed only in static conditions, that is the lighter liquid was merely floating on the heavier liquid when the transfer was taking place from either phase. The data for the two cases are also provided in Tables 31-33.

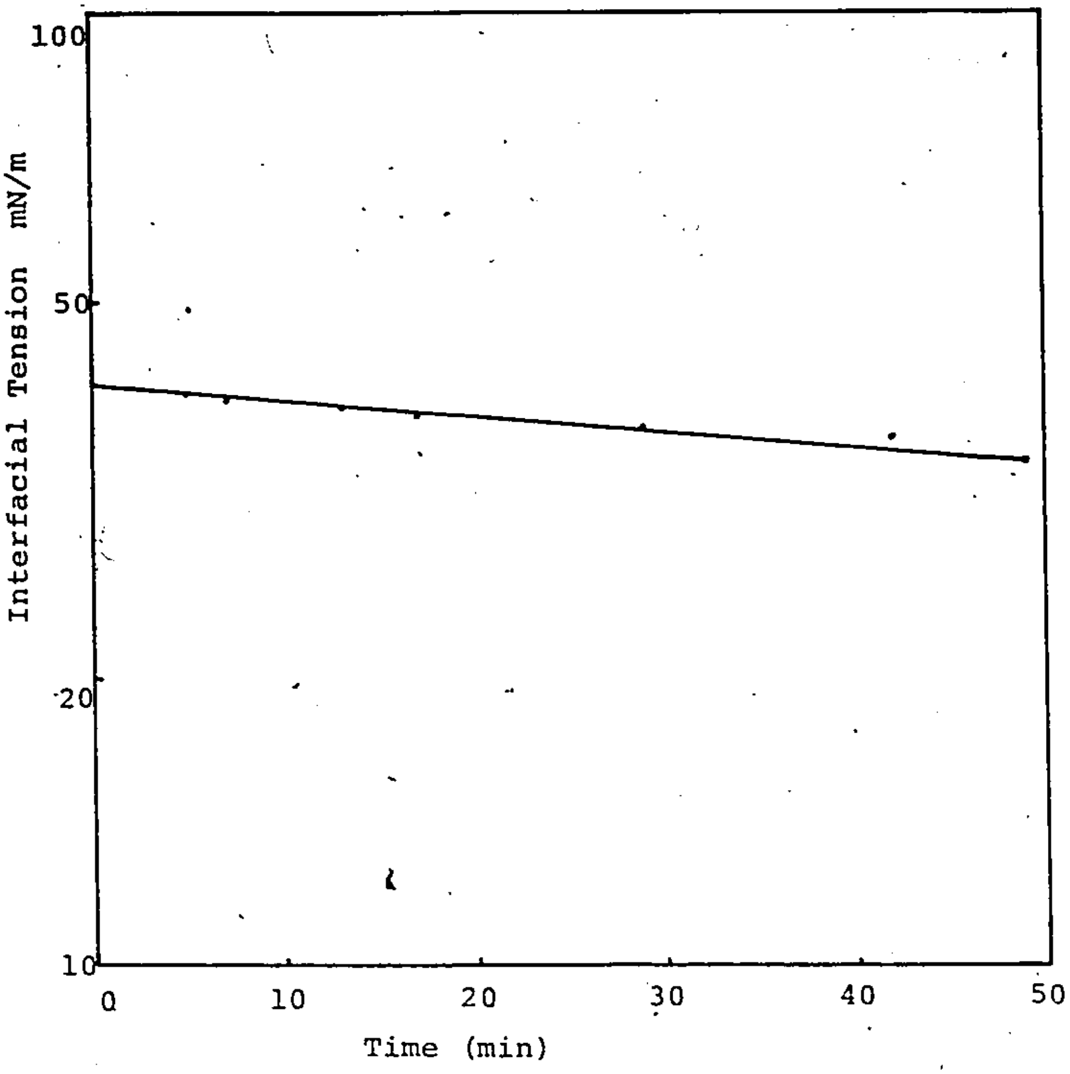


FIGURE 25 Interfacial tension vs time for transfer of iodine from water to n-Heptane

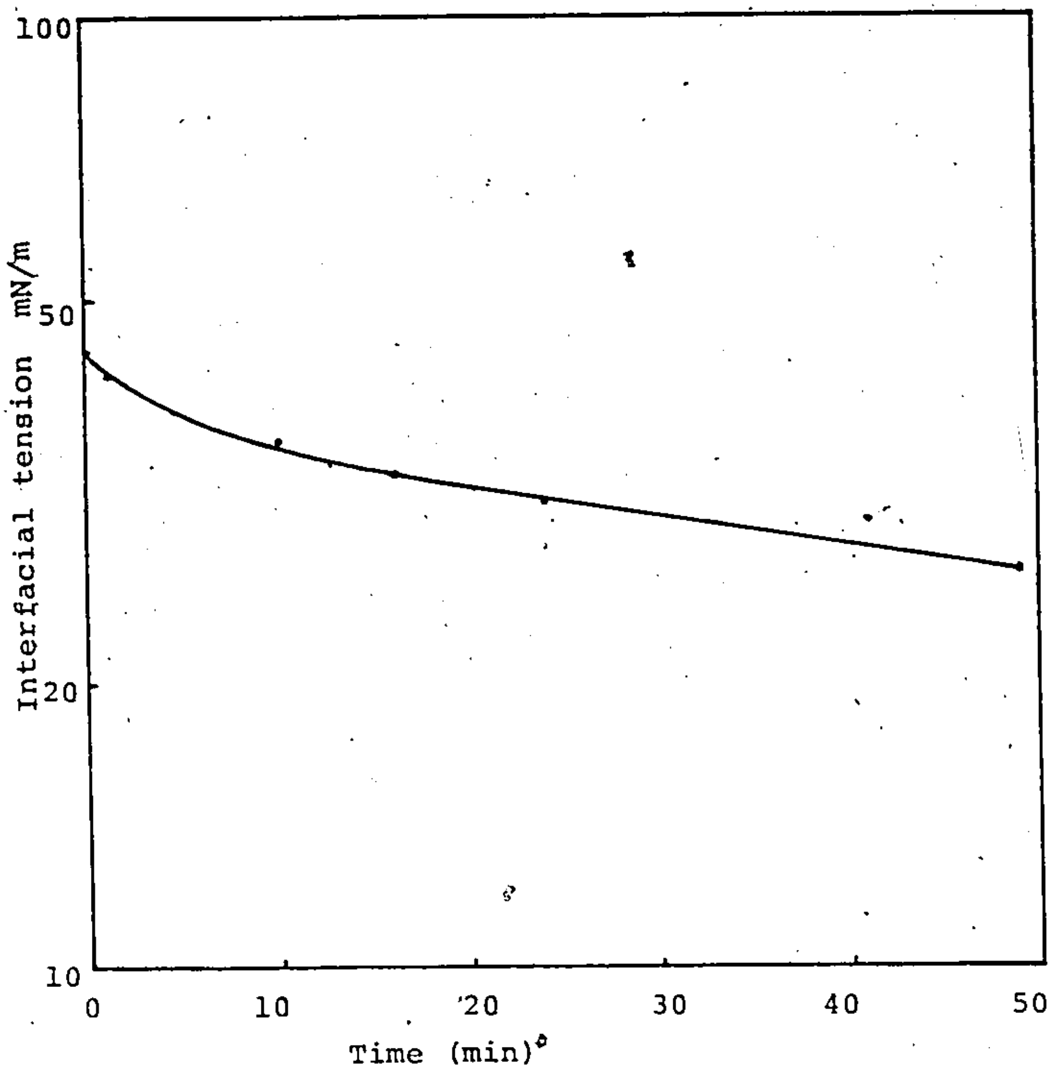


FIGURE 26 Interfacial tension vs time for transfer of iodine from n-Heptane to water.

INTERFACIAL TENSION (σ_i) VARIATION

TABLE 31 σ_i vs t - SOLUTE TRANSFERRING FROM AQUEOUS TO ORGANIC PHASE

Time (min)	σ_i mN/m
0	41
5	40
7	39.5
13	38.5
17	38
29	37
42	36
49	34

TABLE 32 σ_i vs t - SOLUTE TRANSFERRING FROM ORGANIC TO AQUEOUS PHASE

Time (min)	σ_i mN/m
0	44
1	41.5
10	36
12	34
16	33
24	31
41	29.5
49	26

CHAPTER 7

DISCUSSION OF THE RESULTS

In the experiments with reaction between iodine and sodium thiosulphate (Series 1), the experimental mass transfer coefficients for 3 and 6 cm slugs were 0.5475×10^{-5} and 0.279×10^{-5} m/s (Table 3, p. 37). These values were based on the straight line drop of the concentration with time (Fig. 6, p. 35). The corresponding penetration theory values were 11.04×10^{-5} and 6.902×10^{-5} m/s. From this it can be seen that the actual mass transfer rates were very much less than those of the penetration theory. This could possibly be explained from the observations made during the couse of the experiments.

There was a clear 'transparent' zone at the interface always circling around the slug during the transfer. This 'transparent' zone was present due to two effects: the solute at the interface was removed by reaction with thiosulphate in the aqueous phase and there was not enough transfer of the solute from the bulk of the liquid to the interface. Since the original solvent (Kerosene) was highly impure and has no specific composition, the impurities present within it have reduced the diffusion of the solute to such an extent that it overcompensated the instantaneous nature of the reaction.

On the other hand, the coefficients for the initial period in the same experiments were 3.804x10^{-5} and 7.493x10^{-5} m/s respectively. Although the value for 3 cm slug is not equal to that of the penetration theory, the 6 cm slug gave a value close to the predicted value. This is understandable since at the beginning of the experiment the solute near the interface quickly transferred and reacted with the reagent. Subsquently the organic phase film was depleted much faster than the rate of transfer from the bulk of the phase and hence the initial transfer rate was following the theoretical behaviour.

Also, the interesting observation is that the initial mass transfer rate for 3 cm slug was much less than the theoretical value compared to the 6 cm slug case. This is, undoubtedly, due to the effects of 'ends' of the slug. Although overall height of the slug was measured to be 3 cm, tail and nose itself constitute more than two-thirds of the slug thus violating the assumptions made in the derivation of equations for velocity. A 6 cm slug, however, closely follows the assumption of large length/diameter ratio. Further, the velocity profile will not be fully developed at the nose of the slug nor over its short length for 3 cm slug. The same behaviour could be noticed in the next series of experiments in which acetic acid was transferring from Kerosene to water (Series 2).

In experiments with acetic acid (Section 4.2) the coefficient for 4.7 cm slug length was 0.6764×10^{-5} and the 11.7 cm it was 2.7086×10^{-5} m/s (Table 4, p. 42). These were considerably lower than their respective theoretical values, 7.95×10^{-5} and 5.823×10^{-5} m/s. However, the initial period estimates for both lengths of the slugs were close to the penetration theory values thus again confirming the situation described earlier of reduced transfer from the bulk of the phase to the interface. It is encouraging to note that the initial transfer rates are amendable to the theoretical analysis. But this is of little practical use if the later behaviour deviates from theory which can not be explained quantitatively.

In the final run of the experiments (Section 4.3) with the same solvent, Kerosene, the effect of mixing on the transfer rate was observed before switching to n-Heptane as the solvent. Slug length was 3 cm and the concentration-time curves were shown in Fig. 9 (p. 44). The curves show that mixing in fact enhances the mass transfer to the slug, of course if the turbulence caused by insertion of the hypodermic is believed to be less significant. If turbulence was significant, on the contrary, the intake of the solute would be much more than the observed.

The crux of the matter is that mixing inside the slug caused greater transfer which implies that the bulk concentration tended to be uniform. In fact this is true. Without mixing, the laminar velocity profiles inside the slug show that there is a Hadamard type[33] continuous internal circulation without much 'turbulence' or internal mixing inside the slug as in the Handlos and Baron model[34]. This, obviously, would reduce the mass transfer rate to a value lower than if the slug was completely uniform inside the slug, which is the basis for the penetration theory. This was proven further in experiments (Section 4.4) with n-Heptane with 'free'* slugs and slugs 'suspended'* from the disc.

In Series 4, experiments were carried out for three different slug lengths-3,6 and 9 cm, slugs being 'free' inside the tube. The concentration curves were shown in Figs. 12-14 (pp. 49-51). Also shown were curves for suspended slugs, the data of which were taken from Series 6. The figures indicate that mass transfer is greater in suspended slugs than in free slugs. This is because the disc from which slugs were suspended in effect acts as a baffle to the circulatory pattern in the slug and thus breaks up the flow pattern to cause mixing. This mixing

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*For explanation, see Chapter 3.

in turn increases the mass transfer as noted earlier.

The effect of mixing seems to be more in 3 cm slug lengths than in other slug lengths, allowing for differences in aqueous phase concentrations. This could be due to the 'shortness' of the 3 cm slug thus making it resemble more of a sphere when it is free. On the other hand, if the 6 and 9 cm slugs were 'immobile' at the tail end, velocity streamlines would only be confined to the upper position of the slug and thus whatever mixing is caused would not be effective in the lower regions of the slug.

Mass transfer coefficients for free and suspended slugs of the three lengths were given in Tables 5-7 (pp. 54-55). The coefficients for suspended slugs tend to be higher because of mixing inside. However, the coefficients in general were lower by 50% than the theoretical values. The difference was maximum for 3 cm slug lengths because of their geometry, i.e. low length/diameter ratio. The reasons for lower transfer rates could be one or combination of these factors.

(i) As given in Chapter 2, the solvent n-Heptane was at least 98% pure, the remaining 2% may constitute homologous constituents or other hydrocarbons. In any case these impurities play a great role in reducing the transfer rates.

(ii) It was mentioned in Chapter 4 that iodine in the aqueous phase has a negligible reaction with water. The reaction could be given by:

$$I_2 + H_2O \rightleftharpoons HI + HIO$$

$$K = 3 \times 10^{-13} \text{ at } 25^\circ C.$$

This should not alter the results since the aqueous phase solution was preprepared and hence whatever iodine transferred would be fixed . On the other hand, there could be an error in determining the amount of free iodine available by titrating with sodium thiosulphate solution. This is because as iodine reacts with thiosulphate the reaction shifts backward and more iodine would be liberated thus giving a false value. But it can be seen that the extent of reaction is negligible, and since the volume of solution titrated is also small the error would be statistically insignificant.

(iii) Pertaining to the above discussion, it can be argued that the presence of compounds besides iodine might change the diffusivity of iodine. But the solutions are so dilute, the extent of the reaction is small, and also that the effect of diffusivity is only to a fractional power, this can be safely ignored. Further, earlier workers using aqueous solutions calculated the diffusivities by Wilke-Chang[34] correlation as was done in this case also.

However, Freeman and Tavlarides[15] recently observed that the impurities present in the original solvents reduced the apparent diffusivities by one-third and they also observed the impurities being collected at the interface in their jet experiments.

(iv) Referring to the distribution coefficient ($m = 9.412$), it was chosen purely on an intuitive basis that m should correspond to large excess of the aqueous phase. In general the phase ratio should not be a factor in the choice of m. This causes another uncertainty whether the same value of m is applicable throught the duration of mass transfer.

(v) The organic phase, n-Heptane, is not entirely immiscible with the aqueous phase. Its solubility, though, is negligible, (0.005 parts in 100 parts)[31], yet could set in the complex problem of multicomponent diffusion rather than a single component diffusion as has been assumed so far. Finally,

(vi) With the transfer of iodine into the organic phase, the problem becomes one of a varying phase resistance. This is not solvable at this time especially when there is no method to treat even the simpler problem of constant phase resistance for a cylindrical slug in terms of Hadamard stream functions.

These are only some of the possible causes for the low mass transfer rates. Some other causes will be taken up in the following section.

The effect of mixing was also observed in the case of extraction with reaction and this will be discussed at a later stage.

Experiments of Series 6 form the 'core' of the experiments. Herein studied were the effect of slug length and aqueous phase velocity. For slug length 3,6,9 and 12 cms, calculated coefficients were given in Tables 9-24 (pp. 65-72).

The difference in mass transfer coefficients between the penetration theory and the actual values (Tables 9-13, pp. 65-67) is very high and perhaps, attention need not be given to this since the 3 cm slug has a low length/ diameter ratio. The longer slug lengths - 6,9 and 12 cm. - also yielded lower values (Tables 14-24) at the beginning up to 5 mins.

It has to be noted that the closeness between actual and experimental values for longer slugs appears to be generally within the time interval of 5-7.5 mins. This points out that there is some sort of 'delayed' action or 'build-up' effect. There is no reason for this build-up to play a role since the aqueous solution displaces the previously held water film along the surface at the start of the experiment. The possible explanation for this is that the circulatory patterns or mixing inside the slug were not fully operative at the beginning of the experiments. As the time passes by, a steady-state develops in which the circulation aids in greater intake of the solute. Unfortunately, experiments were not carried on beyond the 7.5 mins. interval and hence no data are available to confirm this. It is also important to realize that the individual phase transfer coefficients need not be proportional to $D^{0.5}$ as assumed in the calculation of the coefficients. However, it has been shown that this holds good in most of the cases, as pointed out by Harriot.[38] This has to be confirmed by extensive experimentation.

It is interesting to find if same is the case in the reverse transfer, that is the transfer of iodine from the organic to aqueous phase. The results of the experiments (Series 7) with 6 cm long slug were given in Tables 25-28 (pp. 76-77). It is intriguing to see that the actual coefficients were much less than the theoretical values. Obviously the 'stady-state' hypothesis offered above is not valid here. No attempt was made to check whether the distribution coefficient of 9.412 is still applicable in the present case. Eqn. (26) shows the effect of m on K_o to be negligible. And any lower value of m would reduce the individual coefficients even further.

Keeping the question open to discussion, the answer can be sought in terms of hydrodynamic and surface conditions.

If it is assumed that organic phase has dissolved surface active material, either by dissolving Tygon tube material on its entry to the concentric steel tube or having some foreign material dissolved in itself, then the results of Scholtens et al.[36] might be applicable. They showed that the effect of spread macromolecules on mass transfer is not one of blockage of surface but to be primarily of a hydrodynamic origin. As pointed out in Chapter 2, this is to say that the concentration gradients along the surface create an interfacial tension gradient which opposes the flow of the interface itself.

The system of n-Heptane/Iodine-Water has high interfacial tension (Figs. 25-26, pp. 85-86), unlike the conditions of Baird and Ho[16] who worked with only low interfacial-tension systems. Thus the system readily accepts contamination accompanying the water phase. The contamination would then be collected at the bottom of the slug thereby decreasing the tension there. This opposes the shear of the aqueous phase flow and a balance would thus be established. This rebalancing not only reduces the interfacial velocity but prevents the passage of momentum across the interface which inturn lowers the transfer rates.

Also the fact is that iodine has high molecular weight. Hence it could be more concentrated at the rear of the slug than at the front end by virtue of gravity. It can be seen from Fig. 25 (p. 85) that interfacial tension would be lower at higher concentrations. This could act alone or in combination with the effect of contamination to lower the transfer rates.

Finally, as pointed out earlier, that n-Heptane tries to dissolve in the aqueous phase in the presence of iodine. Thus the dissolution of n-Heptane could reduce the mass transfer rates markedly to much lower values than expected.

In the next series (Section 5.3) of experiments, solute was again transferring from the organic to aqueous phase but with a reaction in the aqueous phase. The system studied was n-Heptane/Iodine-Sodium thiosulphate/Water. Since the reaction is assumed to be instantaneous, resistance lies entirely in the organic phase.

The concentration-time curves for a single slug length and single aqueous phase flow rate for 'free' and 'suspended' cases were shown in Fig. 22 (p. 79) and the mass transfer coefficients in Table 29 (p. 80). The coefficients were 0.5897×10^{-4} and 0.8047×10^{-4} m/s respectively. The corresponding penetration theory values were 1.3462×10^{-4} and 1.326×10^{-4} m/s. Though the transfer rate for suspended slug is much faster than for the free slug, it is still lower than the expected value. The reason could be either a hydrodynamic effect or a violation of the assumption that the reaction was instantaneous. The latter could not be verified since there is no specific condition when the reaction is very fast but with depletion of the solute.

In the last series of experiments (Section 5.4) acetic acid was transferring from n-Heptane to water. Distribution data (Fig. 23, p. 82) show that acetic acid is highly soluble in water, so the resistance to transfer lies wholly in the organic phase. However, the actual mass transfer coefficient tends to be two to three times greater than the expected value. This is also in conformity with experiments reported by Lewis [24] and Bakker et al.[10] This could be easily explained by the nature of the solute. Acetic acid has the tendency to cause Marangoni effects which increase the mass transfer several fold. Sawistowski[37] has tabulated the conditions under which there will be instabilities based on the analysis of Sterrling and Scriven[26]. For transfer from phases 1 to 2 the table gives the conditions for instabilities. These are depicted in Fig. 27.

In the present case:

$$r^2 = \frac{D_1}{D_2} = \frac{\text{Diffusivity of Acetic Acid in n-Heptane}}{\text{Diffusivity of Acetic Acid in Water}}$$

$$= \frac{3.0313 \times 10^{-9}\ \text{m}^2/\text{s}}{1.219 \times 10^{-9}\ \text{m}^2/\text{s}} > 1$$

$$e^2 = \frac{\nu_1}{\nu_2} = \frac{\mu_1}{\rho_1} \times \frac{\rho_2}{\mu_2} = \frac{0.5668 \times 0.9984}{0.6863 \times 0.0101} > 1$$

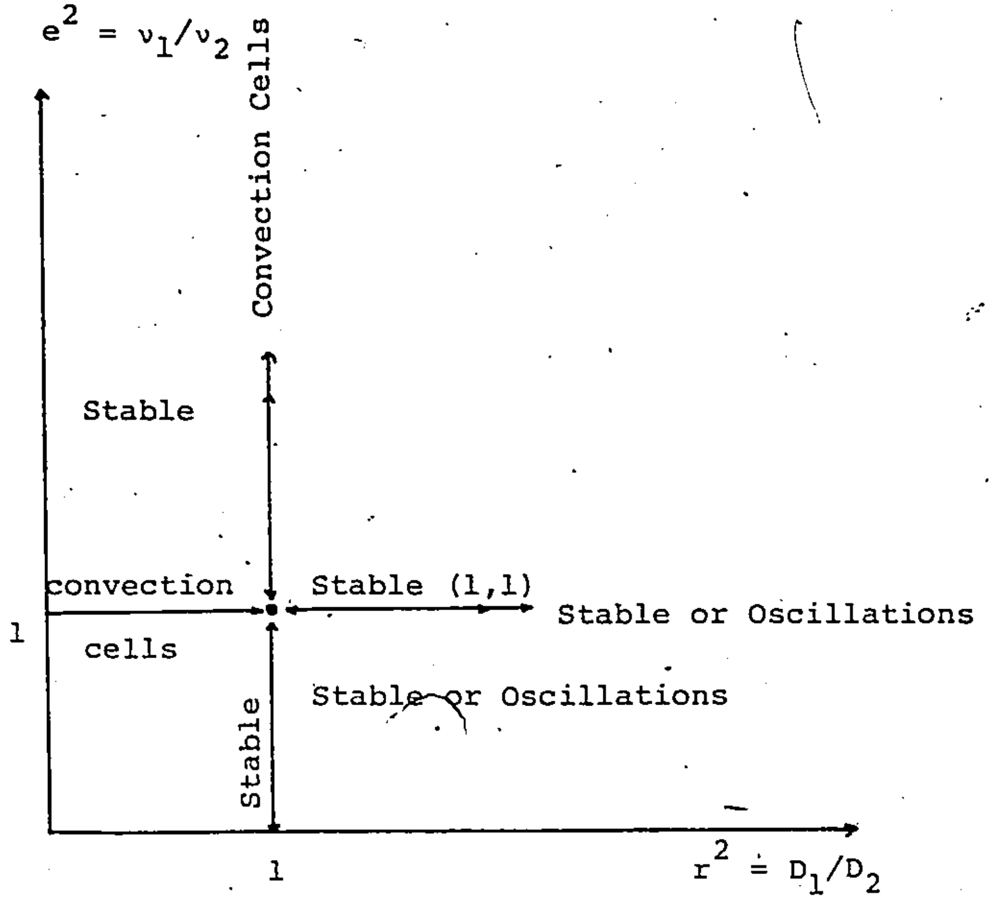

FIGURE 27 Conditions for Occurrence of Instabilities

However, for $r^2 > 1$ and $e^2 > 1$; intuition suggests that oscillations or convection cells are possible. In the experiments of Bakker et al.[10] $r^2 > 1$ and $e^2 < 1$ where they observed excess mass transfer rates.

Finally, the slug technique could be compared to a wetted-wall tower. In both cases there is a thin film adjacent to the tube wall. But the falling film is always laminar and stable in the slug technique whereas it could be turbulent in the wetted-wall tower. The organic phase of the slug resembles the inner "core" fluid of the wetted-wall tower.

Brinsmade and Bliss[31], in experiments with a falling-film apparatus under turbulent conditions, resolved the overall coefficient into individual phase coefficients. They assumed k_o and k_a to be functions of flow rates of the phases in contact and fit the experimental data. However, this is not feasible in the slug technique because both phases have the same Reynolds number at the interface and also the flow rate of the organic phase is undefinable. Thus there can be no further comparison between the two and hence no attempt was made to correlate the data in dimensionless equations.

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

1. Liquid-liquid extraction experiments were carried out with ternary systems on the slug apparatus to assess the usefulness of the technique.
2. The equipment proposed by Baird and Ho[16] could be modified easily to accommodate changes in aqueous phase flow rate.
3. It is shown that the disc in the modified apparatus not only permitted variation in the aqueous phase flow but has enhanced the mass transfer rates by improving the mixing inside the slug and making the slug to be uniform in composition.
4. Though the disc has improved the mass transfer rates for all slug lengths, the improvement was less for longer lengths compared to the shorter lengths. This ineffectiveness was believed to be due to an 'immobile' portion of the rear of the slug.
5. Kerosene could be used in preliminary studies but no conclusions should be based on results with it.
6. The experimental mass transfer coefficients were in general found to be less than the expected values

based on penetration theory for the system n-Heptane-Iodine/Water. But it is believed that there is some 'steady-state' effect, that is the transfer rates tend to be high with the passage of time.

7. Mass transfer coefficients in the 'reverse transfer' (from organic to aqueous) for the same system were much lower than the expected values. This could be due to a single or multiple effects of dissolution of the solvent itself, hydrodynamic conditions, variation of resistance with time, contaminants and uncertainty about the distribution coefficient.
8. Mass transfer coefficients in extraction with reaction (between iodine and sodium thiosulphate) were also lower than the theoretical values. It was not known if this was due to hydrodynamic effects or a violation of the assumption that the reaction was instantaneous.
9. Mass transfer rates with acetic acid as solute tend to be much more than the theoretical values. This was found to be in agreement with the earlier reports and was due to Marangoni effects.
10. Though the slug technique closely resembles the wetted-wall column, individual phase coefficients were not correlated in dimensionless form since the flow rate of the organic phase was undefinable.

It is recommended that a system which has well-defined data of distribution coefficients and diffusivities should be tried on the slug technique. It should be important that the system or conditions of transfer chosen should not induce Marangoni effects. Finally, care should be taken to use only redistilled water and any other solvents. Organic liquids should not be allowed to pass through polymeric materials. If the above cautions are observed, it is believed that the technique could be very useful in obtaining the fundamental data for future use.

NOMENCLATURE

A	Interfacial area, m^2
C	Concentration, moles ℓ^{-1}
C^*	Equilibrium concentration, moles ℓ^{-1}
d	Differential operator
D	Diffusivity, m^2/s
e^2	Ratio of kinematic viscosities in Phases 1 and 2
g	Gravitational constant, m^2/s
k	Film mass transfer coefficient, m/s
K	Equilibrium constant; Over-all mass transfer coefficient, m/s
K_L	Mass transfer coefficient, m/s
L	Length of the slug, mm
m	Distribution coefficient (= concentration in the organic phase/concentration in the aqueous phase)
m'	Square root of the ratio of the diffusivities in aqueous and organic phases
N	Mass transfer rate, moles/m^2s
p'	Pressure gradient (= dp/dz), N/m^3
q	Volumetric flow rate of the aqueous phase, m^3/s
r	Radius, m
r^2	Ratio of diffusivities in Phases 1 and 2

R	Radius of the tube, m
Re	Reynolds number
t	Time, s
U_1, U_2	Integration constants
v	Velocity, m/s
V_s	Volume of the slug, m^3
X	Ratio of concentration in the slug to the product of distribution coefficient and concentration in the aqueous phase.
Z	Direction

GREEK LETTERS

ε	Enhancement factor
ϕ	Dimensionless slug radius
μ	Viscosity, m.Pa.s
ν	Kinematic viscosity, m^2/s
ρ	Density, Kg/m^3
ψ	Viscosity ratio
σ	Interfacial/surface tension, mN/m
τ	Contact time, s

SUBSCRIPTS

a	Aqueous phase
A	Component
b	Bulk
e	Effluent (2nd subscript)
f	Superficial
i	Interfacial

o	First subscript: Organic phase; Second subscript: at time t = 0
s	Slug
v	Average (2nd subscript)
1,2	Instants

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APPENDIX A

CONCENTRATION VERSUS TIME DATA

APPENDIX A

SERIES 1: KEROSENE/IODINE-SODIUM THIOSULPHATE/WATER

TABLE A-1 CONCENTRATION-TIME DATA FOR L = 30 mm

(C_{wo} = 0.0102 M)

Time (min)	Iodine in Kerosene mM
0	10.262
0.5	7.3886
1.5	6.5667
3.0	6.0546
4.5	5.131
6.0	4.4127
10.0	3.4891
12.21	2.4263
15.0	1.6419
22.0	0.8210

TABLE A-2 CONCENTRATION-TIME DATA FOR L = 60 mm

(C_{wo} = 0.01012 M)

Time (min)	Iodine in Kerosene mM
0.	10.262
0.25	6.6703
0.5	5.4693
1.0	5.0797
1.45	4.4127
3.0	4.4126
4.5	4.0022
6.0	3.5917
10.0	2.4628
15.0	1.2879
20.0	0.4618
25.0	0.2566

SERIES 2: KEROSENE/ACETIC ACID (A.A.)-WATER

TABLE A-3 CONCENTRATION-TIME DATA FOR L=47 mm
($C_{s,o}$ = 0.2597 M)

Time (min)	A.A. in Effluent mM
0.833	2.2
1.5	0.78
3.0	0.556
4.5	0.433
6.0	0.30
9.0	0.241
12.0	0.1547
15.0	0.1472
20.0	0.1433
25.0	0.07879

TABLE A-4 CONCENTRATION-TIME DATA FOR L = 117 mm
($C_{s,o}$ = 0.2597 M)

0.5	2.5
1.0	1.5
3.0	0.431
4.5	0.2769
6.0	0.1148
9.0	0.057
12.0	0.0477
15.0	0.0438
20.0	0.0375

SYSTEM: n-HEPTANE/IODINE-WATER

TABLE A-5 CONCENTRATION-TIME DATA (SERIES 7)

Time (min)	Iodine in n-Heptane (mM) v_f: 0.0167 m/s	Iodine in n-Heptane (mM) v_f 0.0109 m/s
0	1.1833	0.7144
5	0.9946	0.6288
10	0.8167	0.5312
15	0.6089	0.4433

TABLE A-6 CONCENTRATION-TIME DATA (SERIES 7)

Time (min)	Iodine in n-Heptane (mM) v_f: 0.0229 m/s	Iodine in n-Heptane (mM) v_f: 0.0287 m/s
0	0.7144	0.7144
5	0.5752	0.5275
10	0.4909	0.4250
15	0.4103	0.3590

SYSTEM: n-HEPTANE/IODINE - SODIUM THIOSUPHATE/WATER

TABLE A-7 CONCENTRATION-TIME DATA (SERIES 8 AND 5)
(C_{wo} : 0.19711 M)

Time (min)	Iodine in n-Heptane, mM	
	Suspended-slug	Free-slug
0	13.336	13.336
0.25	9.594	10.231
0.5	5.7723	6.8073
1.0	2.3089	3.6226
2.0	0.4543	1.1247

SYSTEM: n-HEPTANE/ACETIC ACID - WATER

TABLE A-8 CONCENTRATION-TIME DATA (SERIES 9)

Time (min)	A. A. in n-Heptane, M
0	0.1971
0.317	1.8×10^{-3}
0.5	9.43×10^{-4}
1.0	8.148×10^{-4}
2.0	3.859×10^{-4}
4.0	8.577×10^{-6}