SEPARATION OF n-PARAFFIN HYDROCARBONS
BY THE UREA ADDUCTION PROCESS

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PREFACE

One of the newest separation techniques is the formation of the crystalline inclusion complexes, adducts as they are commonly called, of urea with straight chain saturated hydrocarbons. This technique has already become a useful and powerful tool in petroleum and petrochemical industries. Judging from the number of the patents being issued on separation processes employing urea, it can be assumed that considerable effort is being devoted by oil companies in this direction. As a result, numerous cyclic processes have been proposed. However, very little information is available on the fundamental aspects of the mass transfer and the rate of crystal formation.

The basic purpose of this project was to study the mass transfer and the kinetics aspects of the urea adducts formation. However, there were some preliminary data, such as the solubility of n-paraffins in aqueous acetic acid-isobutanol solutions, which had to be determined. Although a few experiments were performed on the mechanism of the urea adduct formation, a great part of this work is concerned with the determination of the primary data.

I would like to take this opportunity to express my gratitude to Dr. R. N. Maddox and other members of the

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CHAPTER I

INTRODUCTION

Urea selectively crystallizes with organic compounds that have a long straight-chain group to produce a solid filterable complex or adduct*. The principle of urea adducts formation is that; urea molecules form a channel large enough to accommodate straight-chain types of organic compounds, but not cyclic or branched compounds. In some cases urea can form crystalline complexes with long molecules that have an appropriately placed methyl group or a certain terminal mono-cyclic group(5). There is a minimum chain length for urea adducts formation at given temperature. At 25° C, for example, the minimum chain length for n-paraffins is six carbon atoms(30). Therefore the formation of urea adducts is a function of the length of the straight-chain and the cross-section of the organic molecules.

The urea adducts are stable at room temperature and yet they can be decomposed to the original compounds without great difficulty. Dissociation of the urea complexes can be accomplished by heating the crystals to about 130° C or by dissolving the

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* Complex is a substance, ordinarily in crystalline form, consisting of two or more compounds, each one capable of existing by itself. When one of the compounds is contained in the frame work of the other, the frame represents a channel or a cage and the complex is called an inclusion complex.

crystals in water at room temperature. In heating the complex, a layer of hydrocarbon is formed over a layer of melted urea. When the adducts are dissolved in water, a hydrocarbon phase and aqueous urea solution is formed.

The solvent for urea in urea adduction processes is water or some low molecular weight alcohols, such as methyl alcohol. The aqueous solution has the advantage that little urea will dissolve in the organic phase, thus making the recovery of urea simpler and more efficient(6). To improve the rate of crystallization of adducts from aqueous urea solution, the addition of some secondary alcohol such as isobutanol has been recommended(6). Keeping the Ph of the solution below seven by addition of small amount of acetic acid will also favor the rapid formation of urea complexes. The use of methanol as a solvent for urea has been suggested by some early investigators, as: Bengen(1), Zimmerschield(30), Redlich(21), and Schlank(6). The saturated methanol urea solution process can be operated at a lower temperature than the aqueous solution process. The problem of chemical recovery, however, can be overcome by addition of water to methanol. The use of saturated methanol-urea solution has been particularly recommended for laboratory investigations as well as for treating wax and heavy distillate.

Application of Urea Adduction

As one may expect, the most important application of urea adduction is in separation of n-paraffin hydrocarbons from branched, cyclic and aromatic compounds. Normal paraffins can be produced free from branched type as well as oxygen, sulfur and nitrogen compounds present in most crude oil, by the urea extractive crystallization process. Subsequent fractional distillation of the straight-chain saturated hydrocarbons yields individual compounds.

So far there has not been a great demand for normal paraffins, although in the future they may be considered for use as feed stock in preparation of detergents, fatty acids, paint thinners and as solvent in the extraction of vegetable oils(5). The removal of n-paraffins, however, from some petroleum fractions, such as gasoline and kerosene is of great importance. At the present time, from the economical standpoint, urea adduction cannot compete with catalytic reforming.

Since normal paraffins have a low octane number and a relatively high freezing point, the removal of these hydrocarbons from gasoline fractions will improve the octane number. The military requirement of low pour point of kerosene as jet fuel can also be met by removal of n-paraffin from kerosene. By definition, hexadecane has a cetane number of 100. The cetane number of other straight-chain hydrocarbons is also high. Thus, normal paraffin removed from gasoline and kerosene fractions may be added to diesel fuel as a blend for improving the cetane number of diesel fuel.

In thermally cracking heavy petroleum waxes, some straight-chain olefins are produced. Garner(19) describes a method utilizing the urea adduction process for separating these olefin hydrocarbons from cracking products.

Recently there has been considerable interest in the application of urea adduct formation in the dewaxing process. Waxes consisting of a high molecular weight hydrocarbon can be separated from lubricating oil stock at room temperature avoiding the use of refrigeration. Even those waxes from n-paraffin that can escape the removal by low temperature dewaxing processes are crystallized out by the urea adduction method. Therefore, the urea adduction process can produce essentially wax free oil with a low pour point formerly made only from rare wax free crude oil.

Deutche erdoel A. G. of Heide, Germany(11), applies the urea adduction process in producing low pour point oil. An equal volume of oil and aqueous urea (saturated at 160° F) with methylene chloride (for temperature control) are vigorously agitated. The heat of crystallization of urea adducts will vaporize the methylene chloride, keeping the temperature of reaction around 95° F to 115° F. The methylene chloride is condensed and brought back into the reactor. The urea adducts are decomposed by agitation with steam at 170° F giving molten wax and aqueous urea. The Standard Oil Company of Indiana installed a plant in 1956 for production of refrigerator oils, transfer oils and special oils for Arctic services.

Objectives

The primary purpose of this work was to study the mass transfer and the kinetics aspects, and to determine the characteristics of urea adducts formation in agitated suspensions. For this purpose, the following objectives were set up:

1. Conduct a theoretical study of the factors governing

the urea adducts formation.

2. Measure equilibrium data pertaining to the urea adduction.
3. Design a laboratory apparatus and experimentally determine the urea adduction rate.

CHAPTER II

SURVEY OF THE LITERATURE

The rate of the urea adduct formation and the fundamental aspects of the mass transfer across the liquid-liquid interface and from liquid to solid phase has received relatively little direct investigation. In general, for systems such as those used in formation of urea complexes, there are three important factors concerning the mechanism and the rate of crystal formation. These are:

1. Mass transfer across the liquid-liquid interface.
2. Nucleation or formation of the initial adduct crystals.
3. Growth kinetics of the complexes.

Mass Transfer Across the Liquid-Liquid Interface

Among the numerous concepts of mass transfer between two phases, the film theory of Whitman and Lewis(17)(28) and renewal theory of Danckwerts(3) are of great importance.

Whitman and Lewis assumed the existence of a stagment fluid film at the interface which causes a resistance to the mass transfer. It was further assumed that the only way in which solute can pass through the film is by molecular diffusion(17). According to this assumption, the rate of mass transfer can be expressed by the equation:

$$\frac{dw}{d\theta} = (D/X)(C_a - C)A \qquad (1)$$

where:

$\frac{dw}{d\theta}$ = the rate of mass transfer, g.-eq./sec.

D = molecular diffusivity, sq. cm./sec.

X = fictitious film thickness, cm.

A = interfacial area sq. cm.

C = concentration of solution g.-eq./cc.

C_a = interfacial concentration g.-eq./cc.

Danckwerts proposed that instead of assuming the existence of a fictitious film at the interface, the continuous replacement of interfacial surface by the fresh fluid be assumed(4). Thus, a new term, surface-renewal, was introduced. Based on this concept, the mass transfer rate equation, 1, can be written as:

$$\frac{dw}{d\theta} = \overline{DS}^{\frac{1}{2}}(C_a - C) \qquad (2)$$

where:

S = the fractional rate of surface renewal, Sec^{-1}.

It should be noticed that both theories adapted the concentration as the deriving force. Therefore, equations 1 and 2 can be written in a single general form such as:

$$\frac{dw}{d\theta} = K(C_a - C)A \qquad (3)$$

With K as a constant, namely the mass transfer coefficient, equal to D/X in Whitman's equation and $\overline{DS}^{\frac{1}{2}}$ in Danckwerts' equation. Sherwood and Gordon(17), in study of the effect of the molecular diffusivity on the mass transfer coefficient, showed that K, is proportional to D^n, and experimentally found that the value of n is between 0.5 and unity depending on the physical condition of the apparatus and the process under consideration. This is in the fair agreement with equations 1 and 2 in which n is unity and ½ respectively.

Up to the present time there have been very few data published concerning the rate of mass transfer across the liquid-liquid interface for aliphatic compounds and aqueous urea system. There have been, however, some dimensionless correlations such as that which Johnson and Hung(14) obtained in studying the mass transfer coefficient for baffled agitated vessels. They developed the following equation which was developed and used by Sherwood and Gilliland(7) previously:

$$(Kl/D) = N(u/pD)^b \ (rd^2p/u)^c \tag{4}$$

Assuming the Danckwerts' theory of surface-renewal to be correct, they found the exponent of Schmidt number, b, was equal to 0.5. Using equations 2 and 4 the rate of mass transfer can be calculated, provided that the constant N and the exponent c, are known for the system under consideration.

Nucleation or Formation of the Initial Adduct Crystals

The complete causes of crystallization consist of the consecutive processes of nuclei generation and subsequent growth of the nuclei. The initiation of a phase transformation at certain recognizable centers is known as nucleation and the propagation of the transformation from these centers is called growth(19).

A process of crystallization would be described, if the rate of nucleation as well as growth were entirely known.

A number of investigators have developed expressions for nucleation and growth kinetics. Probably the best attempt is one due to Becker and Doering(1). Becker(1) proposed the following equation for nucleation rate.

$$J = e^{-E/kT} e^{-A(T)/kT} \tag{5}$$

where:

J = nucleation rate, number of nuclei formed per unit volume per unit time.

E = activation energy for diffusion.

A(T) = work required to form surface of nucleous.

T = absolute temperature.

k = Boltzman constant.

There are several important points that can be deduced from Becker's equation: the work term A(T) increases with decreasing of supersaturation and is infinite at saturation point. Therefore, the term $e^{-A(T)/kT}$ is zero at saturation. The term $e^{-E/kT}$ increases with increasing temperature. It has been also shown(1) that $e^{-E/kT}$ decreases with increase in supersaturation. The curve J versus temperature has a maximum which corresponds to a definite supersaturation(1). Also it is apparent from the curve J versus temperature that J is low for an appreciable supersaturation, but increases rapidly when a definite supersaturation is reached(17). Finally after a period of time nucleation will occur at any supersaturation.

The growth of the nuclei can be described in the same way as nucleation with the assumption that growth is actually a two dimensional nucleation process(19).

The use of agitated suspensions in crystallization permits operation at high rate crystal production(23). The study of the rate of growth of crystals in agitated vessel has received relatively little direct investigation. The reverse process, however, the dissolution of solids has been studied and the results correlated in terms of dimensionless groups of pertinent variables(14).

Growth Kinetics of Complexes

Consider the reaction between urea and straight-chain hydrocarbons:

$$\text{str.-chain organic compound} + m(\text{urea}) \longrightarrow \text{urea complex}$$

the rate of reaction at any time is given by the following equation:

$$\frac{d(\text{complex})}{d(\text{time})} = K_R(\text{str.-chain})\ (\text{urea})^m - K_P(\text{complex})$$

In the formation of urea adducts, chemical equilibrium is established the same way as in any ordinary chemical reaction(5). When the rate of formation of the complex becomes equal to the rate of decomposition, that is, when the chemical equilibrium is established, the above equation can be expressed as:

$$K_\theta = \frac{(\text{str.-chain})\ (\text{urea})^m}{(\text{complex})} = \frac{K_P}{K_R}$$

or:

$$K_\theta = \frac{({}^a\text{str.-chain})\ ({}^a\text{urea})^m}{{}^a\text{complex}}$$

in which (a) is the activity of the corresponding compound. Since the complex is present as a solid the activity of the complex is equal to unity, and also, since the reactant is present in a separate liquid phase the activity of the straight chain compound is equal to one. Therefore K_θ, the equilibrium constant is a function only of urea concentration(5). In the case of n-paraffin hydrocarbons, the value of K_θ decreases as the chain length increases, indicating the greater formation of complexes that contain longer organic molecules(5).

The degree of dissociation of urea adducts in contact with water depends on the concentration of urea in an aqueous solution. A complex is stable in aqueous solution, if the concentration of urea exceeds a certain value called the decomposition concentration. This can be seen easily by remembering the dependence of equilibrium constant, K_θ, on the activity of urea.

The formation of urea adduct is an exothermic process which exhibits a heat of reaction about the same as or greater than the heat of vaporization of the reactant molecules. The relationship between the equilibrium constant, K_θ, and the temperature and the heat of formation can be expressed by the following equation:

$$-\frac{H}{R} = \frac{d(\ln K_\theta)}{d(1/T)}$$

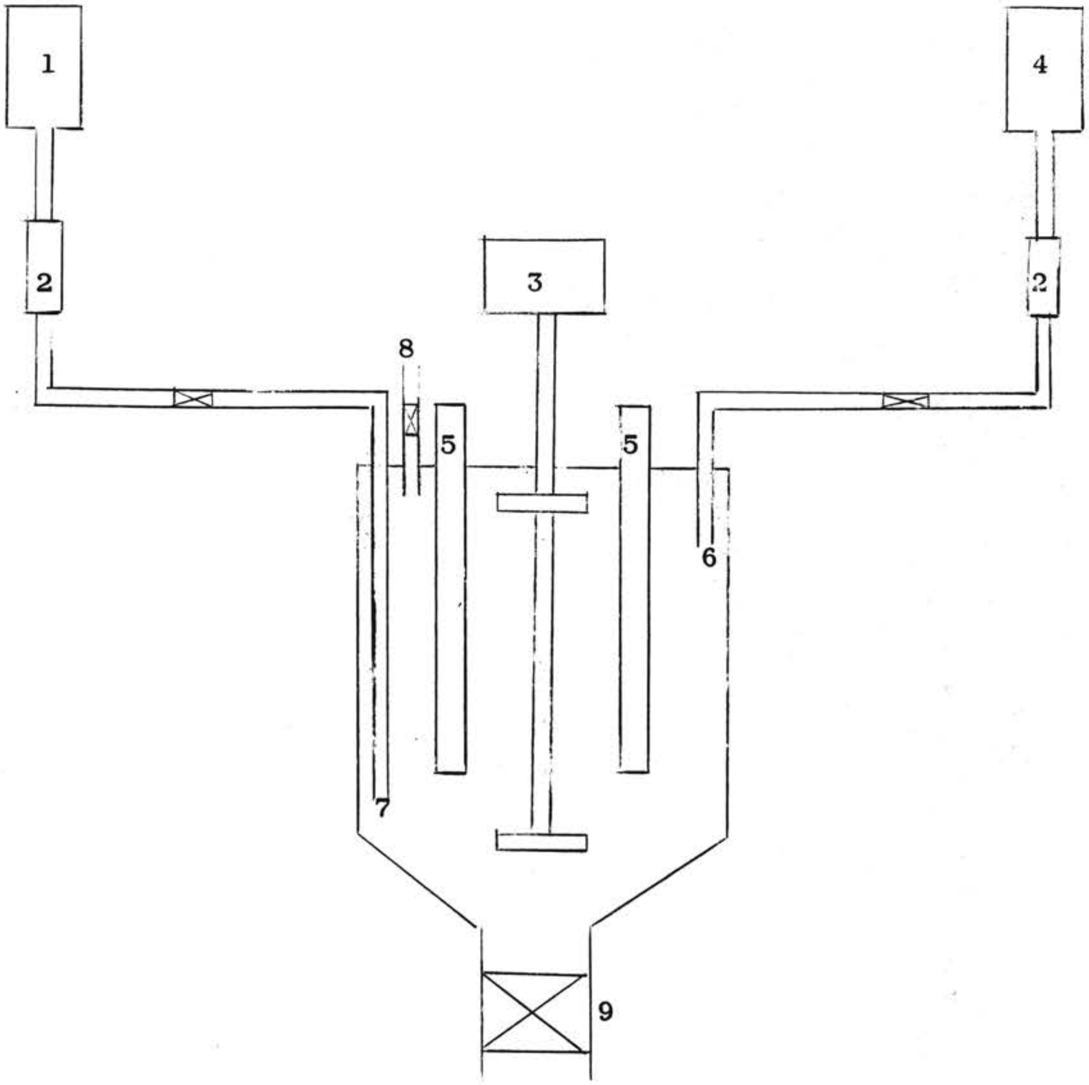
where R is the universal gas constant.

CHAPTER III

EXPERIMENTAL APPARATUS AND PROCEDURE

The original equipment consisted of a Pyrex cylinder with a capacity of approximately two gallons (Figure 1). Two steel plates, one as the top and one as the bottom, completed the extraction vessel. There was a tin funnel soldered to the bottom plate which facilitated the collection of the crystals during the experiments. Two electric strip-heaters combined with two additional baffles assured good agitation. Two constant head tanks each with capacity of four gallons were provided. These tanks served as the charge tank for the organic and aqueous solution. A rotameter was used in the aqueous solution line for flow control of the aqueous solution.

The equipment was designed for a continuous operation. It was found that a continuous process would not be feasible, unless the aqueous urea phase was supersaturated to the point of becoming a slurry. This supersaturation could not be accomplished, unless the urea solution was saturated at a temperature of 170° F. Since extraction was carried out at a temperature of approximately 80° F, the temperature control problem complicated the apparatus designed beyond a reasonable limit. As a result, the experiments, performed at room temperature, were semi-batch employing a conventional packed column.



1. Aqueous Urea Solution Constant Head Tank
2. Rotameters
3. Mixer
4. Organic Head Tank
5. Electric Heaters
6. Organic Inlet
7. Urea Solution Inlet
8. Organic Outlet
9. Urea Complexes Outlet

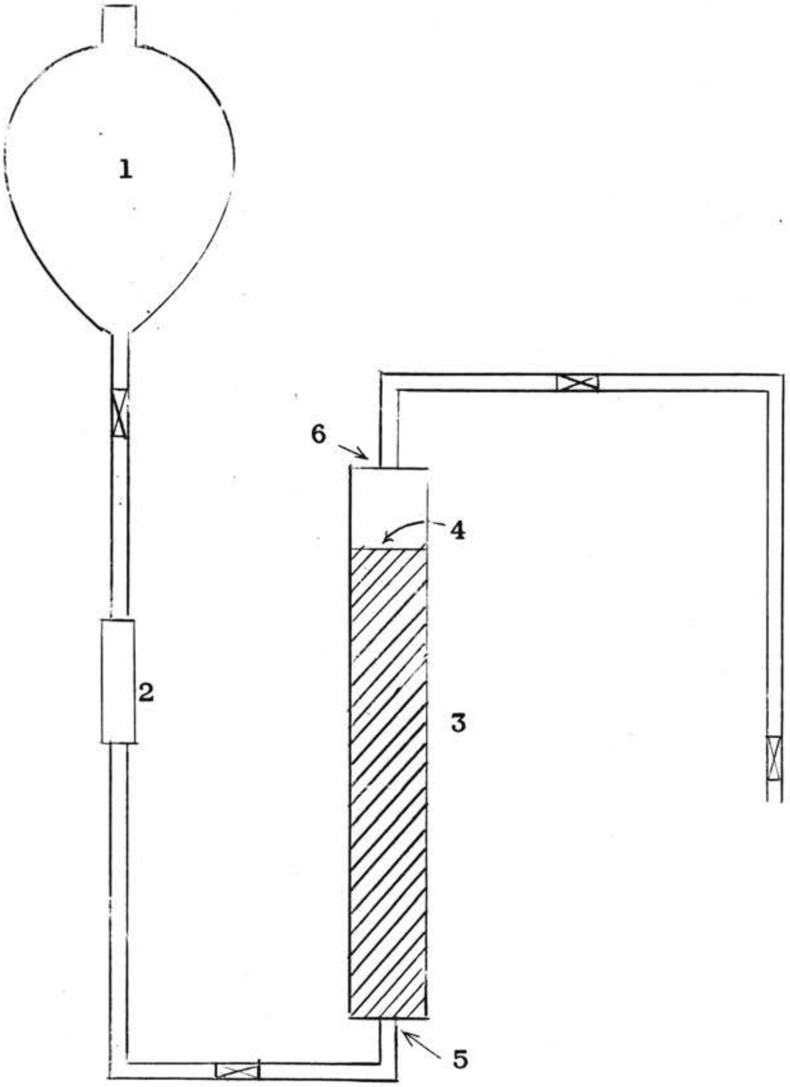
Figure 1. Schematic Drawing of Agitated Reactor for Urea Complex Formation

The column used was 40 centimeters long, 4.20 centimeters in diameter and was packed with Berl saddles. Hydrocarbon entered the column from the bottom and passed upward through saturated urea solution and left the column from the top. A four liter separatory funnel was used as a constant head tank (Figure 2).. A rotameter was placed in the hydrocarbon line for hydrocarbon flow rate control. Pyrex glass tubing and Tygon tubing connections were used.

The equipment for determination of the solubility of n-paraffins in water and equilibrium concentration of n-octane were as follows:

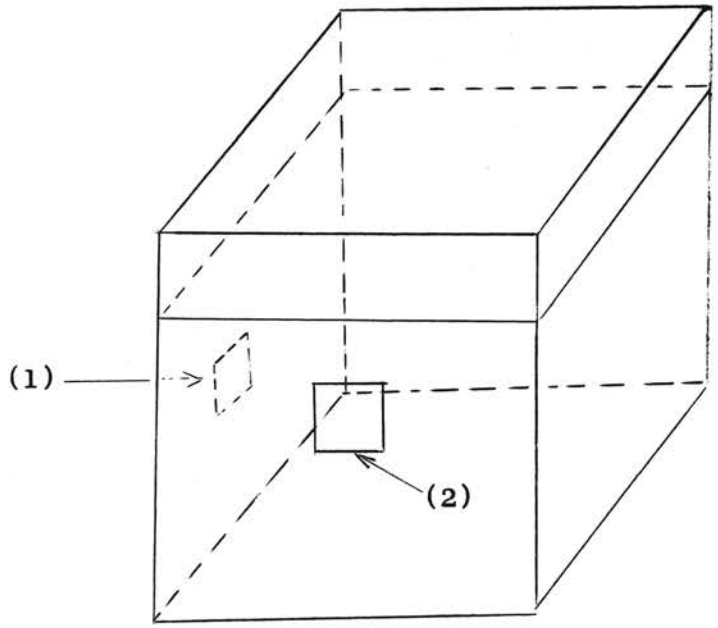
1. A burette graduated to 0.02 cc.
2. Five Erlenmeyer flasks varying from 125 ml. to 750 ml. in capacity.
3. Two "Sergeant" magnetic stirrers with Teflon coated magnetic bars.
4. One 10 λ (10^{-6} l.) syringe.
5. A "Precision Scientific Company" constant temperature bath.

In addition to these, a special carboard box (Figure 3) was designed and built for determination of saturation point of the aqueous solution. The inside of the box was covered with black paper. There were two openings on the two adjacent walls with their axes perpendicular to each other. A light source was placed in the opposite side of one opening. The behavior of the aqueous solution could be observed through the other opening.



1. Constant Head Tank
2. Rotameter
3. Extraction Column
4. Berl Saddle Packing
5. Hydrocarbon Inlet
6. Hydrocarbon Outlet

Figure 2. Schematic Drawing of Packed Column Used in Studies of Urea Adduct Formation



1. Light Inlet Opening
2. Observation Opening

Figure 3. Special Box Designed for Solubility Measurements

Experimental Procedure

Measurement of Solubilities of Pure Hydrocarbon in Water, Additives Solution

The first attempt to measure the solubilities of n-paraffins in water plus additives involved adding a measured volume of pure hydrocarbon on the top of a measured volume of isobutanol-acetic acid solution. The original two gallon glass container was to be used. Three hundred cc of hydrocarbon was added to 7.26 liter of water plus additives (isobutanol and acetic acid) and the interface level was noted. After agitating the organic-water mixture for 24 hours and allowing mixture to settle and separate into two phases, the change in the interface location was noted. From the change of the interface position, the amount of hydrocarbon dissolved in water could be calculated. Since the solubilities of n-paraffins in water are relatively low, there was not a considerable change in the position of the interface. Furthermore, the effect of small change in temperature on the volume of water solution as well as on the volume of hydrocarbon could not be neglected. Due to a large volume of water involved in the experiment, a variation of 0.02° F in temperature would cause a serious error in the results. Consequently, the following method, which is a modification of cloud point method, was used.

A small volume of heptane (0.001 cc, at a time) was added to a measured volume of water plus additives, by means of 10 λ syringe. The solution was stirred for one hour and then placed in a constant temperature bath for about two hours. The solution was mixed periodically manually without taking the flask, containing the solution, out of the constant temperature bath. It was then placed in special designed box (Figure 3). If the solution was saturated, the reflection of light through the solution could be seen through the observation opening of the box. In the case of unsaturated solution, no reflection occurred, and, therefore, no light could be seen through the opening. Additional hydrocarbon would be added, if necessary, until the solution was saturated.

The same procedure was followed for water containing different percentages of isobutanol, and for a one per cent acetic acid solution containing different percentages of isobutyl alcohol. The solubilities of n-octane, n-nonane and n-decane were also determined by the same procedure.

Determination of the Solubility of Urea in Water-Additives Solution

A measured weight of pure urea crystals was added to a measured volume of water plus additives. The solution was mixed thoroughly and the closed top Erlenmeyer flask, containing the solution was placed in a constant temperature bath at a temperature of 27.1° C. This temperature was chosen because the original equipment was to be operated at 27.1° C. The flask was shaken periodically without taking it out of the constant temperature bath. Extra urea was added, from time to time, if it was necessary. After a period of approximately 24 hours, the solution was filtered and undissolved urea was dried and weighed.

While the percentage of acetic acid was held constant to one per cent, the solubility of urea was determined in three, four, five, six and seven per cent isobutanol solutions. The second series of the experiments were run without acetic acid in the solutions. The percentages of isobutanol ranged from three per cent to seven per cent in these different runs.

Determination of Equilibrium Concentration of n-Octane in Aqueous Urea Solution

Pure n-octane was added, by means of 10 λ syringe, to a solution of 10 per cent urea and five per cent isobutanol. The solution was stirred by a magnetic stirrer for five to ten minutes, then placed in a constant temperature bath at a temperature of 27.1° C for two hours. The flask containing the solution was then placed in the special designed box. The light source was turned on and the solution was slowly stirred by the magnetic stirrer. The equilibrium point was reached when urea adduct crystals formed in the solution. If there had not been a trace of urea adducts in the solution, additional n-octane would have been added. The same procedure was followed, until small urea adduct crystals could be observed in the solution.

The same procedure was followed for the determination of equilibrium concentration of n-octane in 20, 30, 40 and 50 per cent urea solution. The percentage of isobutanol was kept constant (five per cent) for all cases.

Determination of Over-all Rate Constant

Before each experimental run for the determination of the over-all rate constant of absorption, $\mathcal{K}$, of hydrocarbons by saturated urea solution, the rotameter had to be calibrated for the hydrocarbon to be used in the experiment. Fresh Berl saddle packing was used for each experiment.

The column was filled to the upper two inch section with saturated urea solution containing five per cent isobutanol and one per cent acetic acid as additives. Above the urea solution fresh organic phase was added up to the overhead outlet. The height of hydrocarbon-aqueous urea solution interface was measured and marked. Then, the hydrocarbon from the constant head tank was bubbled through the urea solution with approximately constant inlet flow rate. The hydrocarbon leaving the column was collected over the interval of five minutes and the average outlet flow rate was calculated. The height of the interface was also measured in five minute intervals, and the outlet flow rate was corrected for the difference in the height of the interface. The rate of absorption of the hydrocarbon by urea solution was obtained by subtracting the hydrocarbon outlet flow rate from the hydrocarbon inlet flow rate.

The above procedure was applied to three runs with normal octane at different inlet flow rates, one run using n-heptane, and one run with n-nonane.

Chemicals

Normal paraffin hydrocarbons ranging from heptane to decane were used in the study of urea adducts formation. The purity of these hydrocarbons was between 95 to 99 mole per cent and they were used as received from Phillips Petroleum Company. Pure urea crystals and once distilled city tap water were used in making up the urea aqueous solution. Glacial acetic acid and isobutyl alcohol were used as the additives for urea aqueous solution.

CHAPTER IV

THEORETICAL CHARACTERISTICS OF THE EQUIPMENT

A modification of equation 3 may give an adequate explanation of what takes place in the column. The equation:

$$\frac{dw}{d\theta} = KA(C_a - C) \qquad (3)$$

as described earlier, relates the rate of mass transfer to the difference between the interfacial concentration, C, and the concentration of the solution, C_a.

The amount of hydrocarbon absorbed by the saturated urea solution in the column per unit time can be related to the concentration difference of hydrocarbon in the urea solution as follows:

$$\frac{1}{V}\frac{dv}{d\theta} = \frac{F_1 - F_2}{V} = K(C_i - C_b) \qquad (9)$$

where:

F_1 = inlet hydrocarbon flow rate, cc/min.

F_2 = outlet hydrocarbon flow rate cc/min.

v = cc hydrocarbon absorbed by saturated urea solution.

V = volume of urea solution in the column

C_i = maximum amount of hydrocarbon which can be absorbed by one ml. of saturated urea solution plus the equilibrium concentration of the hydrocarbon in aqueous solution.

C_b = g. hydrocarbon absorbed per unit volume (ml.) of urea solution in the column at any time.

K = over-all coefficient.

The theoretical value of C_b is:

$$C_b = \rho \int_0^{\theta} \frac{F_1 - F_2)}{V} \, d\theta \tag{10}$$

ρ being the density of the hydrocarbon in question. The value of C_b is of course, equal to the area under the curve $(F_1 - F_2)/V$ versus time.

The maximum concentration, C_i can be calculated by the following equation developed by Kobe and Damask$^{(5)}$.

$$m = 0.6848(n - 1) + 2.181 \tag{11}$$

where:

m = the molar ratio of urea to hydrocarbon.

n = the number of carbon atoms in the hydrocarbon molecule.

therefore:

$$C_i = \frac{NM}{mV} + C^* \tag{12}$$

where:

N = the moles of urea in the column.

M = the molecular weight of the hydrocarbon.

C^* = the equilibrium concentration of the hydrocarbon in urea solution.

V = volume of urea solution in the column.

Maximum concentration, C_i, can also be obtained in the same manner that C_b is obtained, that is:

$$C_i = \rho \int_0^{\infty} \frac{F_1 - F_2}{V} \, d\theta \tag{13}$$

The only difference is that, C_i is the area under the curve $(F_1 - F_2)/V$ versus time from zero to infinity, but C_b is the area under the curve from zero to a definite time.

Equations 9, 10 and 11 were used to calculate the value of κ from experimental results. Substituting the value of C_b from equation 9, and solving for κ results in the following equation:

$$\kappa = \frac{F_1 - F_2}{V} \cdot \frac{1}{C_i - \rho \int_0^{\infty} \frac{(F_1 - F_2) \, d\theta}{V}} \tag{14}$$

as it appears from the above equation κ is a function of the difference between the inlet and outlet flow rates as well as time.

Despite the absorption of hydrocarbon, the volume of saturated urea solution is approximately constant during the experiment. The value of C_i is, of course, constant for a given hydrocarbon. As time increases C_b increases, and, therefore, κ increases with time. During the constant absorption rate period, which starts about fifteen minutes after the experiment has started, κ is a function of time only and increases with time. Conversely, when the absorption rate starts decreasing, the term $(F_1 - F_2)/V$ decreases, but the term $1/\left[C_i - \quad (F_1 - F_2)d\theta/_V\right]$ is still increasing. Apparently the effect of decrease in

$(F_1 - F_2)/V$ on κ is larger than the effect of $1/(C_i - C_b)$. Therefore, κ starts decreasing with time, as it is shown from the graphs of κ versus time for heptane, octane and nonane (Figures 5, 9, 12).

As it was pointed out previously, κ obtained from equation 14 is an over-all rate constant. Therefore, it may not describe any of the possible mechanisms that take place individually. The difficulty is that $(C_i - C_b)$ would not be the correct driving force of any of the possible individual mechanisms that are taking place. Mass Transfer, for example, would involve the driving force for the solubility of hydrocarbon in the water additives solutions minus the actual concentration of hydrocarbon in the aqueous phase. On the other hand, adducts formation would depend upon the supersaturation, that is, the difference between the actual concentration of the hydrocarbon in the aqueous phase and the equilibrium value for the adducts.

Assuming that there are no urea molecules at the hydrocarbon-water interface, the rate of mass transfer from the surface of the hydrocarbon droplets to the bulk of aqueous solution can be expressed by the following equation:

$$\frac{dw}{d\theta} = K_{ma}(C_1 - C_o) \qquad (15)$$

where:

C_1 = the solubility of hydrocarbon in solution of water and additives.

C_o = the bulk concentration of hydrocarbon.

K_{ma} = the mass transfer coefficient.

TABLE I

OVERALL COEFFICIENT FOR n-OCTANE AVERAGE FLOW

RATE 13.5 AT TEMPERATURE 25° C

Time Min.	F_1 cc/min	F_2 cc/min	L Cm	V cc	$F_1 - F_2$ cc/min	$\frac{(F_1 - F_2)10^3}{V}$	C_b X 10^3	C* X 10^3	(C* - C_b)10^3	K X 10^3
5	13.60	13.10	32.2	300	0.50	1.67	5.84	185.5	179.7	9.29
10	12.81	12.00	32.2	300	0.81	2.70	15.25	185.5	170.2	15.9
15	13.80	12.80	32.0	297	1.00	3.33	21.01	185.5	164.5	19.4
20	13.75	12.81	32.0	297	0.94	3.15	32.00	185.5	153.5	20.8
25	13.60	12.61	32.0	297	0.99	3.34	43.30	185.5	142.2	23.5
30	13.60	12.58	32.1	299	1.02	3.41	54.90	185.5	130.6	25.6
35	13.60	12.56	32.1	299	1.02	3.41	66.70	185.5	118.8	28.1
40	13.60	12.80	32.1	299	1.04	3.46	78.5	185.5	107.0	31.8
45	13.80	13.08	32.1	299	1.00	3.33	90.1	185.5	95.5	34.9
50	14.10	13.10	32.2	300	1.02	3.40	101.6	185.5	83.9	39.7
55	14.00	13.15	32.2	300	0.90	3.00	110.5	185.5	75.0	40.0
60	14.10	12.40	32.2	300	0.85	2.73	120.0	185.5	65.5	41.7
65	13.20	12.60	32.2	300	0.80	2.67	129.4	185.5	56.1	47.6
70	13.20	12.60	32.2	300	0.60	2.00	136.3	185.5	49.2	46.8
75	13.20	12.60	32.2	300	0.60	2.00	143.2	185.5	42.48	46.7
80	12.80	12.30	32.2	300	0.50	1.62	148.0	185.5	37.5	44.5
85	12.80	12.35	32.2	300	0.45	1.50	153.2	185.5	32.3	46.4
90	12.80	12.40	32.2	300	0.40	1.33	157.9	185.5	27.6	48.2

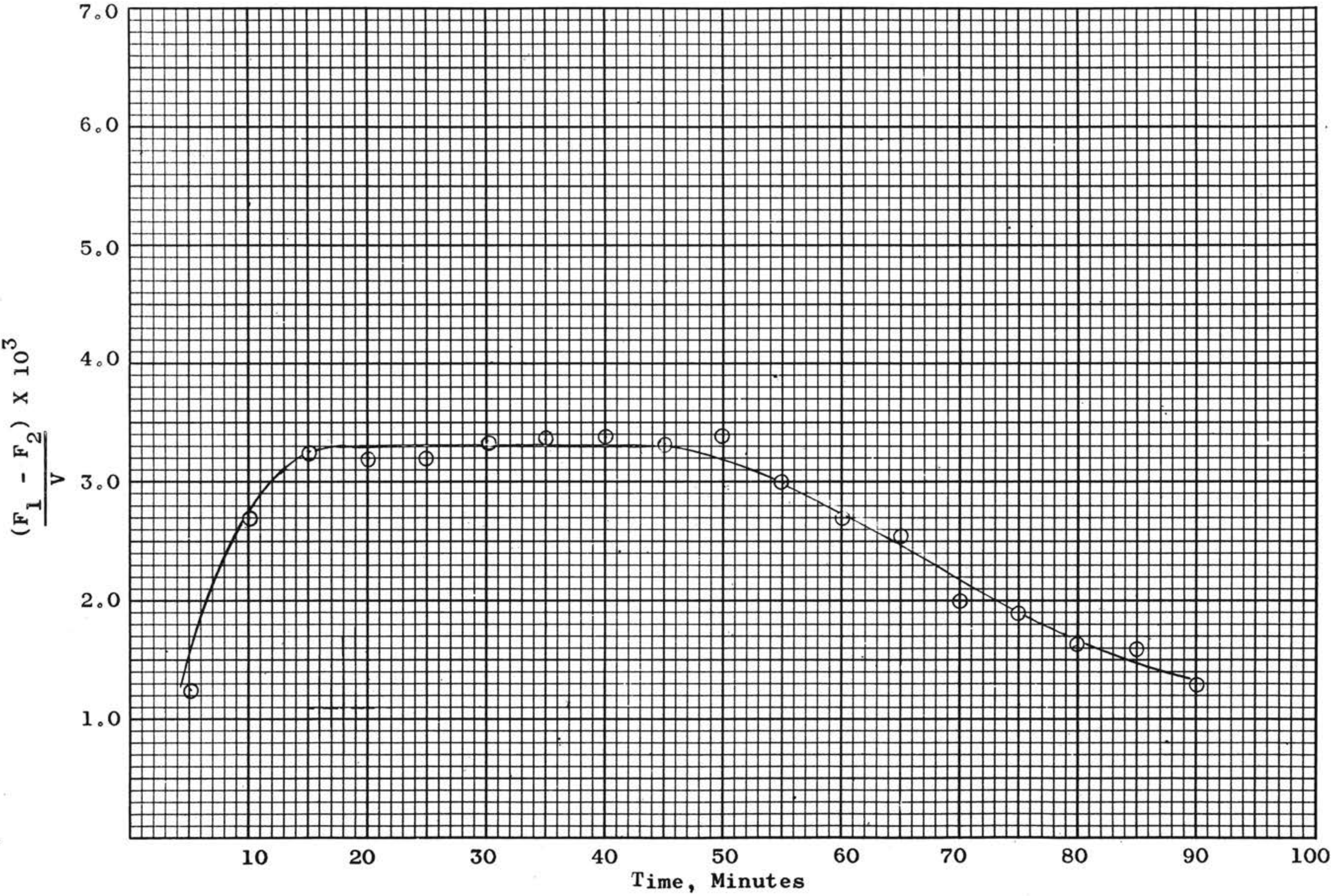


Figure 4. Rate of Absorption of n-Octane in Saturated Urea Solution, $F_1 = 13.5$

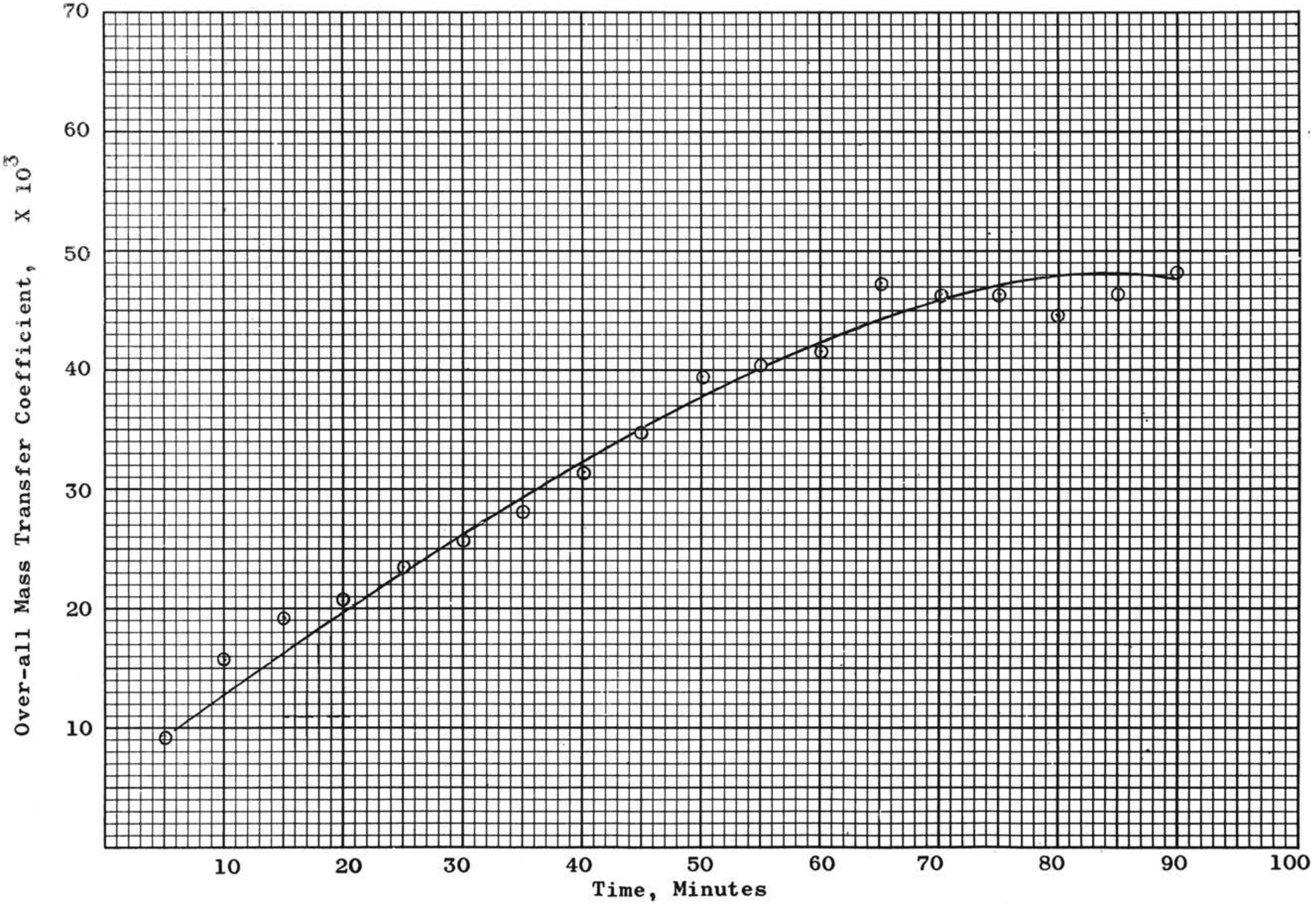


Figure 5. Variation of Over-all Mass Transfer Coefficient for n-Octane, F_1 = 13.5 cc/Min.

TABLE II

OVERALL COEFFICIENT FOR N-OCTANE AVERAGE FLOW RATE 3.95 AT TEMPERATURE 25° C

Time Min.	F_1 cc/min	F_2 cc/min	L Cm	V cc	$F_1 - F_2$ cc/min	$\frac{(F_1 - F_2)10^4}{V}$	C_b X 10^3	C* X 10^3	(C* - C_b)10^3	K X 10^3
5	3.80	3.50	32.5	300	0.30	10.0	3.49	185.5	182.0	5.50
10	3.80	3.35	32.5	300	0.45	15.0	8.72	185.5	176.8	8.50
15	3.95	3.35	32.6	300	0.60	20.0	14.58	185.5	170.4	11.70
20	3.95	3.20	32.6	302	0.75	24.9	23.29	185.5	162.2	15.75
25	3.95	3.10	32.6	302	0.85	28.1	33.13	185.5	152.2	18.4
30	3.95	3.03	32.6	302	0.92	30.4	43.77	185.5	141.8	21.4
35	3.95	3.00	32.7	304	0.95	31.2	54.63	185.5	130.9	23.8
40	3.95	3.00	32.7	304	0.95	31.2	65.53	185.5	120.0	26.0
45	3.95	3.00	32.7	304	0.95	31.2	76.4	185.5	109.1	28.6
50	3.95	3.01	32.6	302	0.94	31.1	87.23	185.5	98.27	31.6
55	3.95	3.00	32.6	302	0.95	31.2	98.13	185.5	87.37	35.7
60	3.95	3.01	32.7	304	0.94	31.2	108.8	185.5	76.70	40.3
65	3.95	3.10	32.6	302	0.85	28.1	117.4	185.5	68.10	41.3
70	3.95	3.20	32.6	302	0.75	24.9	126.5	185.5	59.00	42.0
75	3.95	3.30	32.6	302	0.60	19.8	133.4	185.5	52.1	38.0
80	3.95	3.45	32.6	302	0.50	16.6	139.2	185.5	46.3	35.8
85	3.95	3.50	32.6	302	0.45	14.9	144.6	185.5	40.9	36.4
90	3.95	3.60	32.6	302	0.35	11.6	148.6	185.5	36.9	31.4
95	3.95	3.67	32.6	302	0.28	9.33	151.9	185.5	33.6	27.8
100	3.95	3.73	32.5	300	0.20	6.77	154.2	185.5	31.3	21.6
105	3.95	3.73	32.5	300	0.20	6.77	156.6	185.5	28.9	23.4

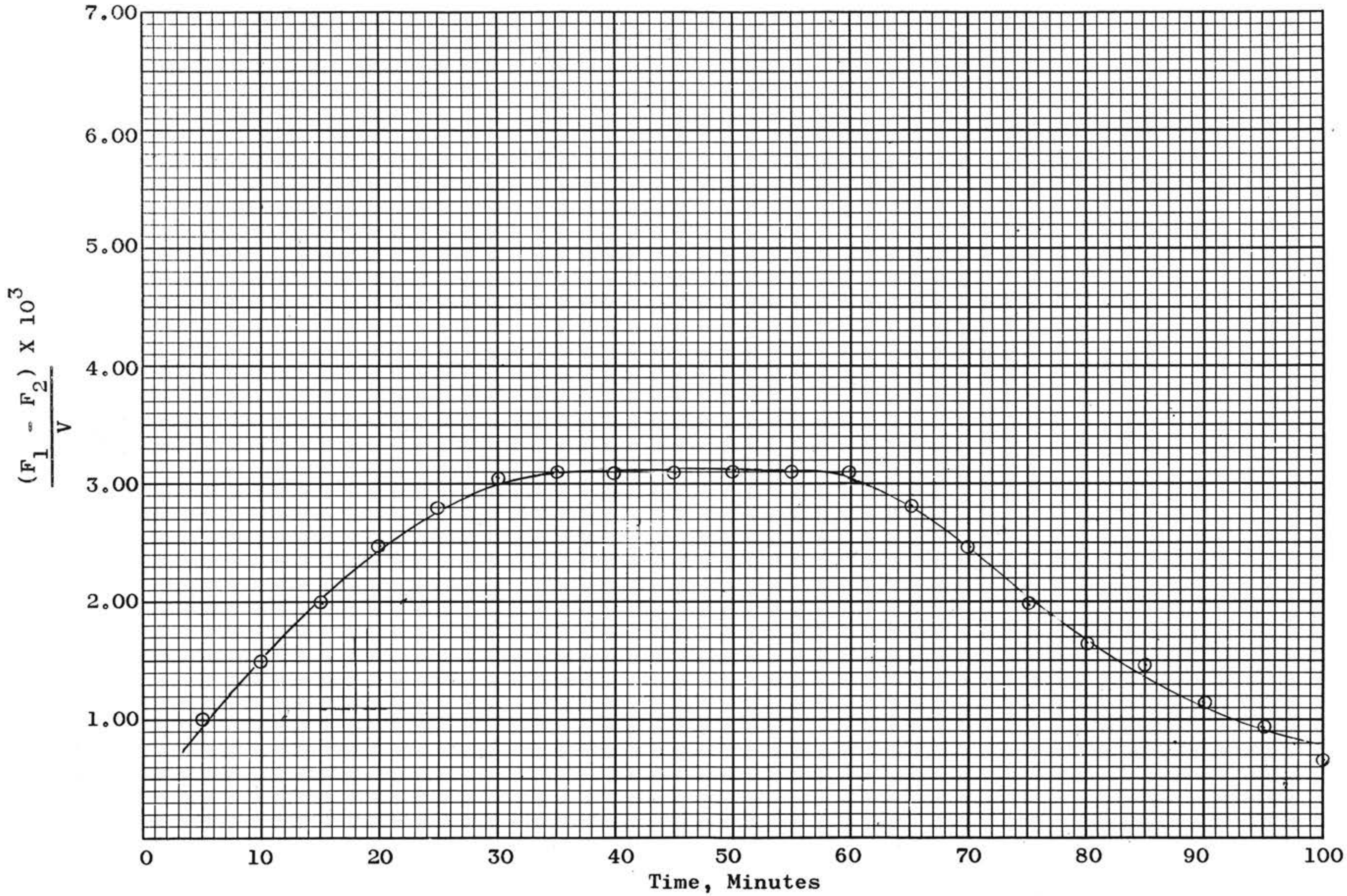


Figure 6. Rate of Absorption of n-Octane in Saturated Urea Solution, F_1 = 3.95 cc/min.

TABLE III

OVERALL COEFFICIENT FOR OCTANE, AVERAGE FLOW RATE OF 19.8 AT 25° C

Time Min.	F_1 cc/min	F_2 cc/min	L Cm	V cc	$F_1 - F_2$ cc/min.	$\frac{(F_1 - F_2)10^3}{V}$	$C_b \times 10^3$	$C^* \times 10^3$	$(C^* - C_b)10^3$	$K \times 10^3$
5.00	18.50	18.00	33.0	300	0.50	1.67	5.85	185.5	179.6	9.29
10.00	27.32	25.30	33.4	305	0.80	2.62	14.91	185.5	170.6	15.4
15.00	20.25	19.45	33.4	305	0.80	2.62	27.21	185.5	158.3	16.6
20.00	19.80	18.73	33.4	305	1.07	3.51	39.81	185.5	145.7	24.1
25.00	19.80	18.70	33.4	305	1.10	3.61	52.41	185.5	133.1	27.1
30.00	19.80	18.70	33.4	305	1.10	3.61	65.01	185.5	120.5	30.0
35.00	19.80	18.70	33.4	303	1.07	3.47	77.61	185.5	107.9	33.4
40.00	19.80	18.71	33.4	305	1.09	3.58	90.21	185.5	95.3	37.8
45.00	19.80	18.70	33.4	305	1.10	3.61	102.8	185.5	82.7	43.6
50.00	19.80	18.90	33.4	305	0.90	2.95	113.4	185.5	72.1	40.1
55.00	19.80	18.95	33.4	305	0.85	2.79	123.2	185.5	62.3	44.8
60.00	19.80	19.05	33.4	305	0.75	2.46	131.8	185.5	53.7	45.8
65.00	19.80	19.20	33.4	305	0.60	1.97	138.7	185.5	46.8	42.1
70.00	19.80	19.30	33.4	305	0.50	1.64	144.4	185.5	41.1	39.9
75.00	19.80	19.30	33.4	305	0.50	1.64	150.2	185.5	35.3	46.4
80.00	19.80	19.45	33.4	305	0.35	1.15	154.2	185.5	31.3	36.7
85.00	19.80	19.55	33.4	305	0.25	0.832	157.2	185.5	28.3	29.4
90.00	19.80	19.60	33.4	305	0.20	0.656	159.5	185.5	26.0	25.2
95.00	19.80	19.60	33.4	305	0.20	0.656	161.8	185.5	23.7	27.7

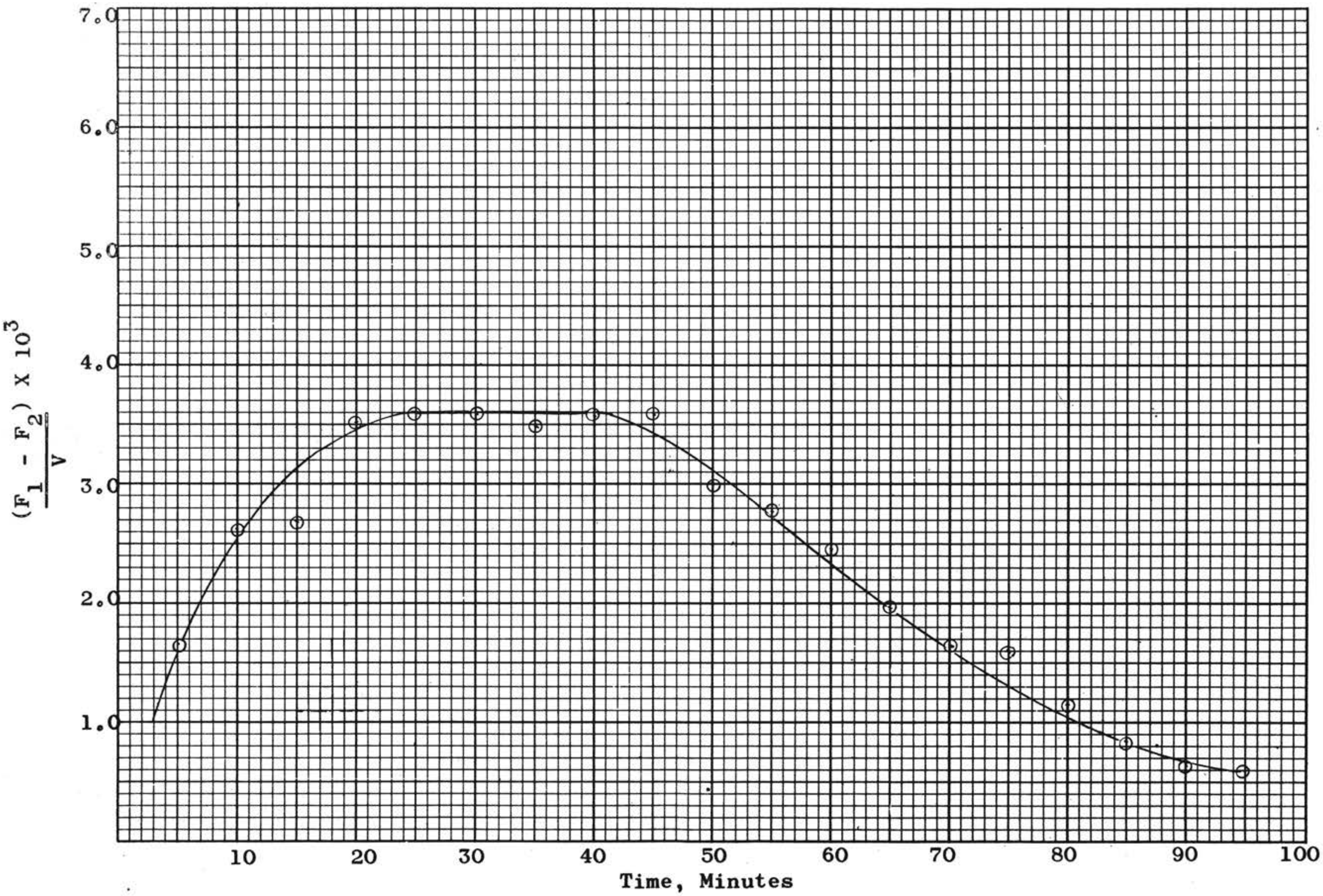


Figure 7. Rate of Absorption of n-Octane in Saturated Urea Solution, F_1 = 19.8 cc/Min.

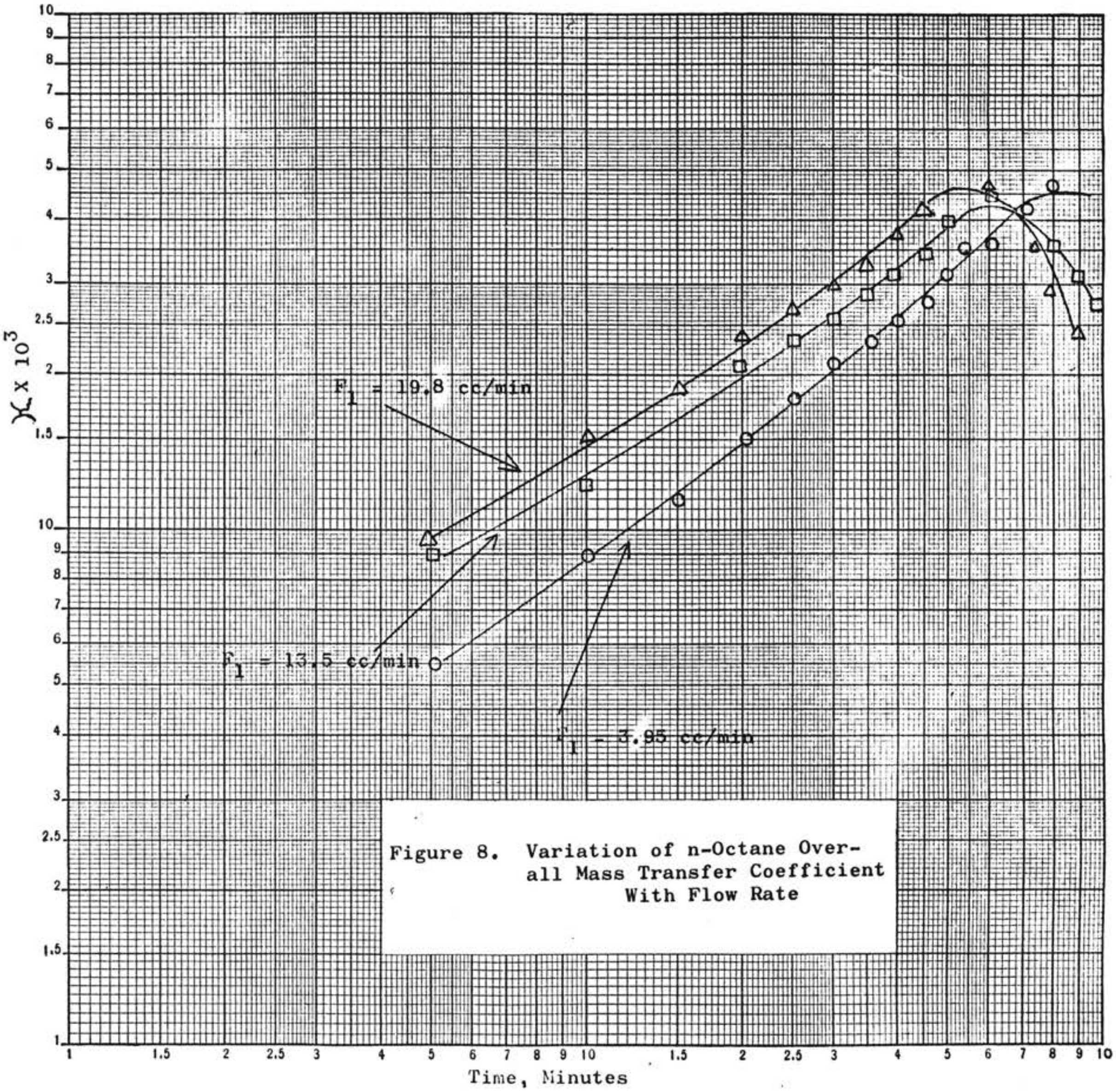


Figure 8. Variation of n-Octane Overall Mass Transfer Coefficient With Flow Rate

TABLE IV

OVERALL COEFFICIENT FOR HEPTANE, AVERAGE FLOW RATE OF 13.2 AT 25° C

Time Min.	F_1 cc/min	F_2 cc/min	L Cm	V cc	$F_1 - F_2$ cc/min	$\frac{(F_1 - F_2)10^3}{V}$	$C_b \times 10^3$	$C^* \times 10^3$	$(C^* - C_b)10^3$	$K \times 10^3$
0.00	0	000	32.0	300	----	----	----	-----	-----	----
5.00	13.95	13.65	32.0	300	0.30	1.00	3.40	178.7	175.3	5.60
10.00	14.00	13.50	32.0	300	0.50	1.67	9.08	178.7	169.6	9.85
15.00	12.80	12.10	32.0	300	0.70	2.33	17.00	178.7	161.7	14.4
20.00	12.80	11.82	32.0	300	0.98	3.23	27.9	178.7	150.8	21.4
25.00	13.00	12.00	31.8	297	1.00	3.36	39.5	178.7	139.2	24.1
30.00	12.10	11.10	31.8	297	1.00	3.36	51.1	178.7	127.6	26.3
35.00	12.10	11.10	31.8	297	1.00	3.36	62.7	178.7	116.0	29.0
40.00	12.30	11.30	32.0	300	1.00	3.34	74.1	178.7	103.9	32.1
45.00	12.20	11.21	32.0	300	0.99	3.30	85.3	178.7	93.4	35.3
50.00	11.98	11.12	32.0	300	0.86	2.87	95.1	178.7	83.6	34.3
55.00	12.60	11.95	32.0	300	0.65	2.17	102.5	178.7	76.2	28.5
60.00	12.30	11.80	32.0	300	0.50	1.67	107.2	178.7	71.5	23.4
65.00	14.10	13.70	32.0	300	0.40	1.33	111.5	178.7	67.2	19.8
70.00	14.50	14.24	32.0	300	0.26	0.87	114.0	178.7	64.7	13.4
75.00	14.50	14.28	32.0	300	0.22	0.74	116.5	178.7	62.2	11.2
80.00	14.06	13.86	32.0	300	0.20	0.70	118.9	178.7	59.8	11.7
85.00	14.00	13.86	32.0	300	0.20	0.70	121.3	178.7	57.4	12.2

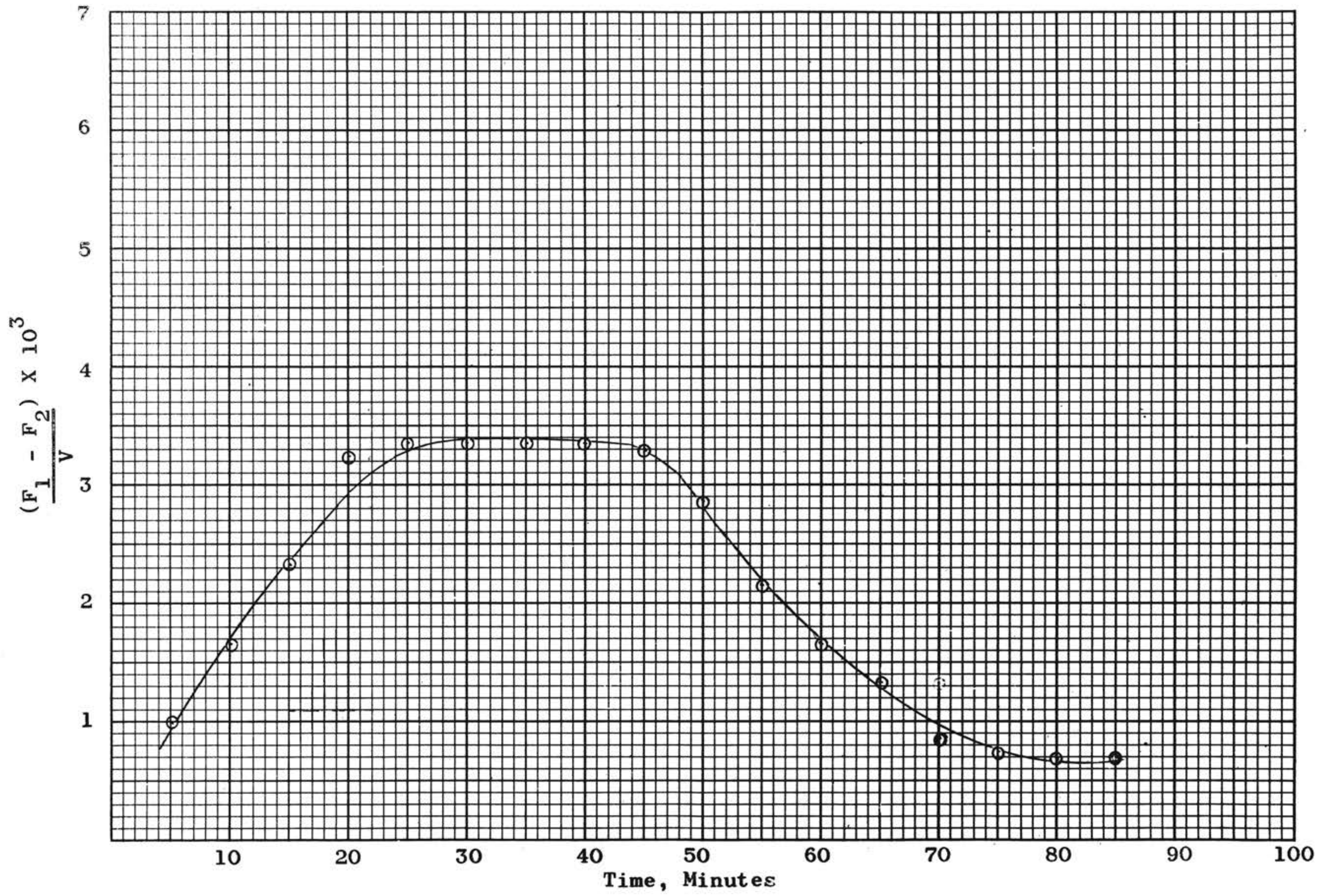


Figure 9. Rate of Absorption of **n-Heptane** in Saturated Urea Solution, F_1 = 13.2 cc/Min.

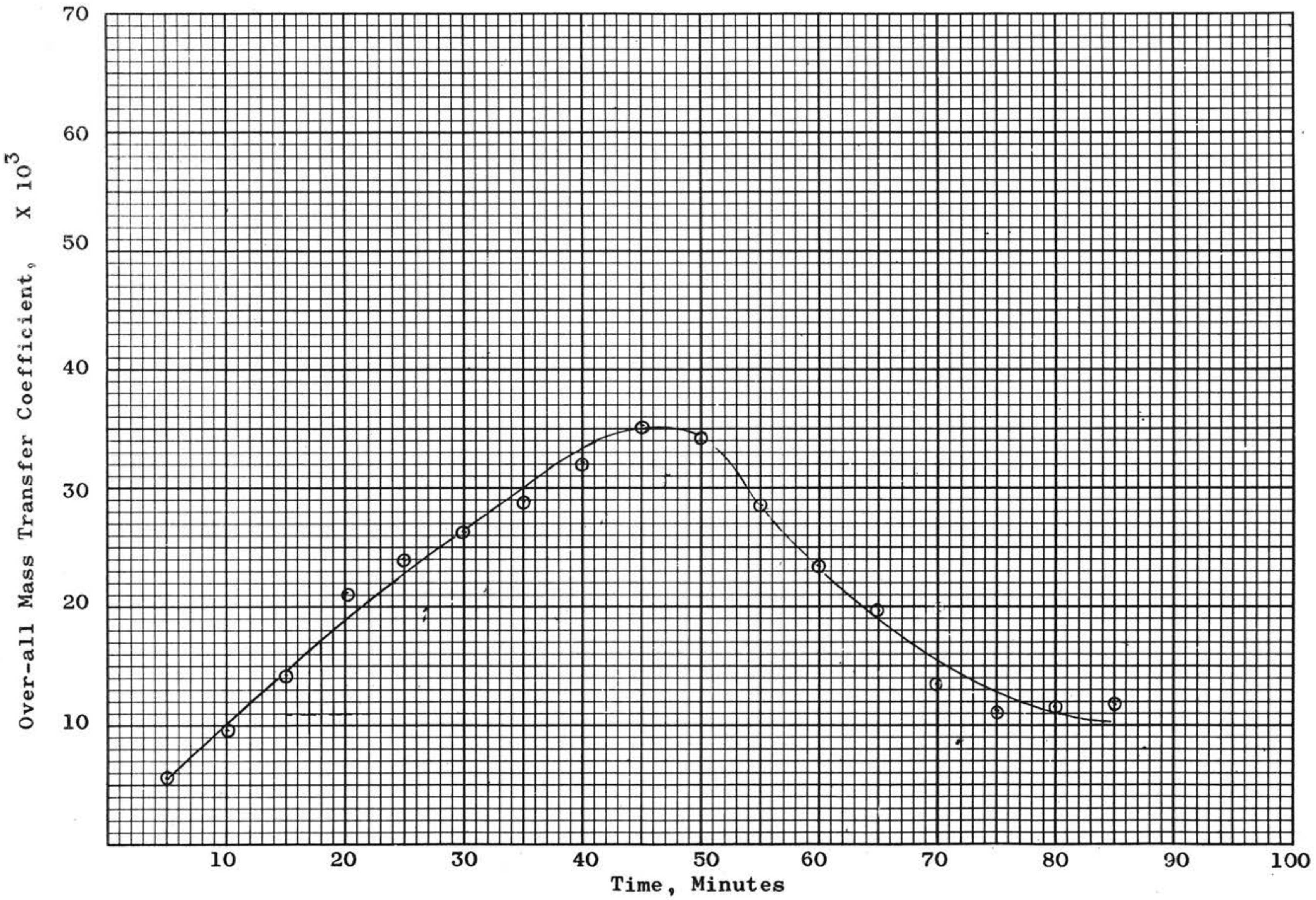


Figure 10. Over-all Mass Transfer Coefficient for n-Heptane

TABLE V

OVERALL COEFFICIENT FOR NONANE, AVERAGE FLOW

RATE 5.60 AT 25° C

Time Min.	F_1 cc/min	F_2 cc/min	L Cm	V cc	$F_1 - F_2$ cc/min	$\frac{(F_1 - F_2)10^3}{V}$	C_b X 10^2	C* X 10^2	(C* - C_b)10^2	κ X 10^2
0.00	0.0	0.0	30.8	300	----	----	-----	-----	-----	----
5.00	6.10	5.42	30.8	300	0.68	2.26	0.805	19.85	19.04	1.17
10.00	5.90	5.00	30.8	300	0.90	3.00	1.87	19.85	17.98	1.67
15.00	5.80	4.60	30.8	300	1.20	4.00	3.13	19.85	16.72	1.87
20.00	5.65	4.60	30.8	300	1.05	3.50	4.37	19.85	15.48	2.26
25.00	5.65	4.60	30.8	300	1.05	3.50	5.56	19.85	14.29	2.45
30.00	5.65	4.60	30.8	300	1.05	3.50	6.82	19.85	13.03	2.69
35.00	5.65	4.60	30.8	300	1.05	3.50	8.06	19.85	11.79	2.97
40.00	5.55	4.50	30.8	300	1.05	3.50	9.34	19.85	10.51	3.33
45.00	5.55	4.55	30.8	300	1.00	3.33	10.5	19.85	9.35	3.56
50.00	5.55	4.63	30.8	300	0.92	3.07	11.5	19.85	8.35	3.68
55.00	5.55	4.66	30.9	302	0.89	2.94	12.5	19.85	7.35	4.00
60.00	5.55	4.68	31.0	303	0.87	2.87	13.4	19.85	6.45	4.45
65.00	5.55	4.73	31.0	303	0.82	2.71	13.9	19.85	5.95	4.55
70.00	5.55	4.80	31.0	303	0.75	2.47	14.5	19.85	5.35	4.62
75.00	5.55	4.82	31.0	303	0.73	2.40	15.4	19.85	4.45	5.39
80.00	5.55	4.85	31.0	303	0.70	2.31	15.7	19.85	4.15	5.57
85.00	5.55	4.81	31.0	303	0.74	2.41	16.0	19.85	3.83	6.26
90.00	5.50	5.00	31.0	303	0.50	1.65	16.5	19.85	3.35	5.28
95.00	5.30	4.90	31.0	303	0.40	1.32	16.80	19.85	3.05	5.25
100.00	5.30	4.95	31.0	303	0.35	1.15	17.30	19.85	2.55	5.89

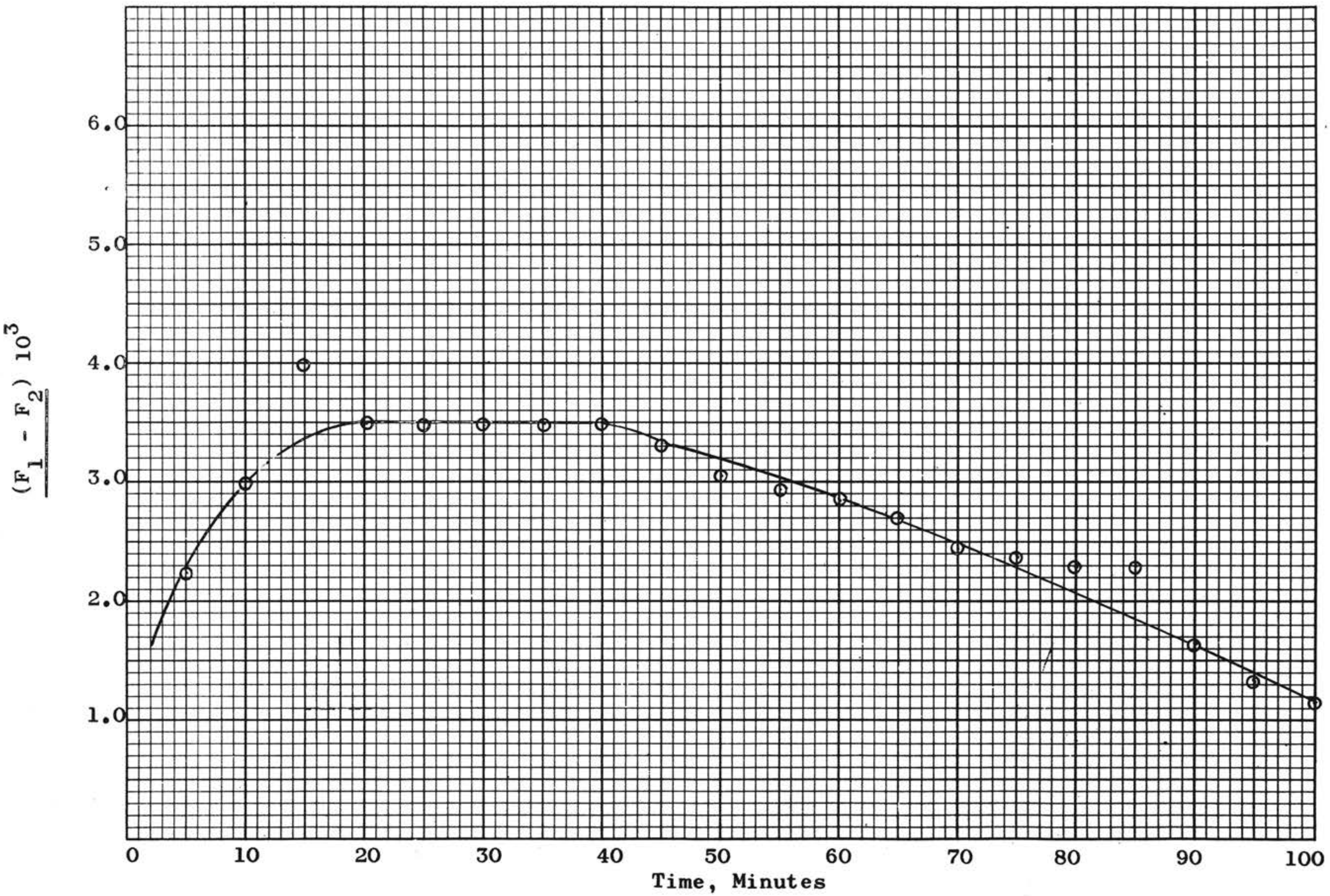


Figure 11. Rate of Absorption of n-Nonane in Saturated Urea Solution, F_1 = 5.60 cc/min.

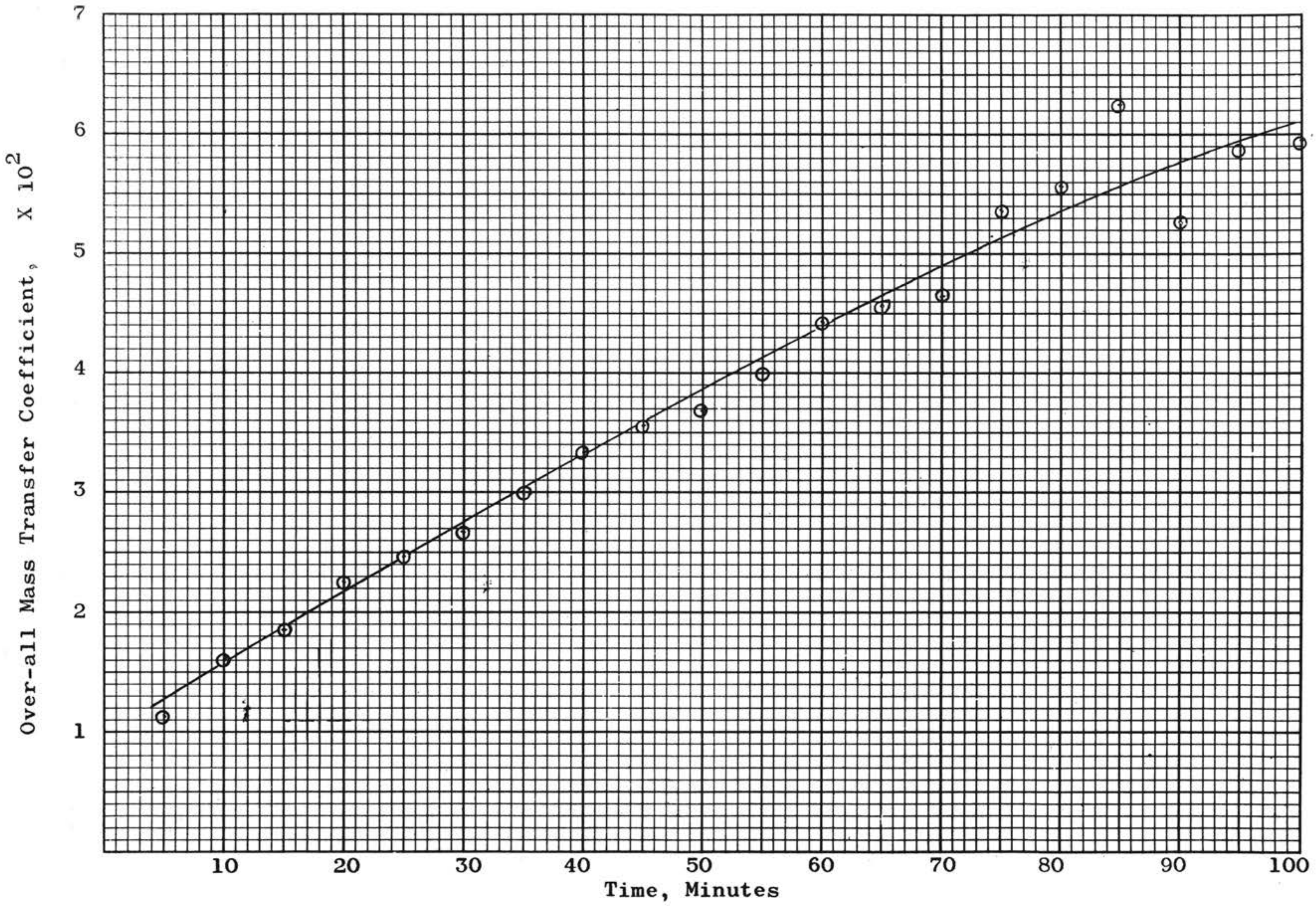


Figure 12. Over-all Mass Transfer Coefficient for n-Nonane

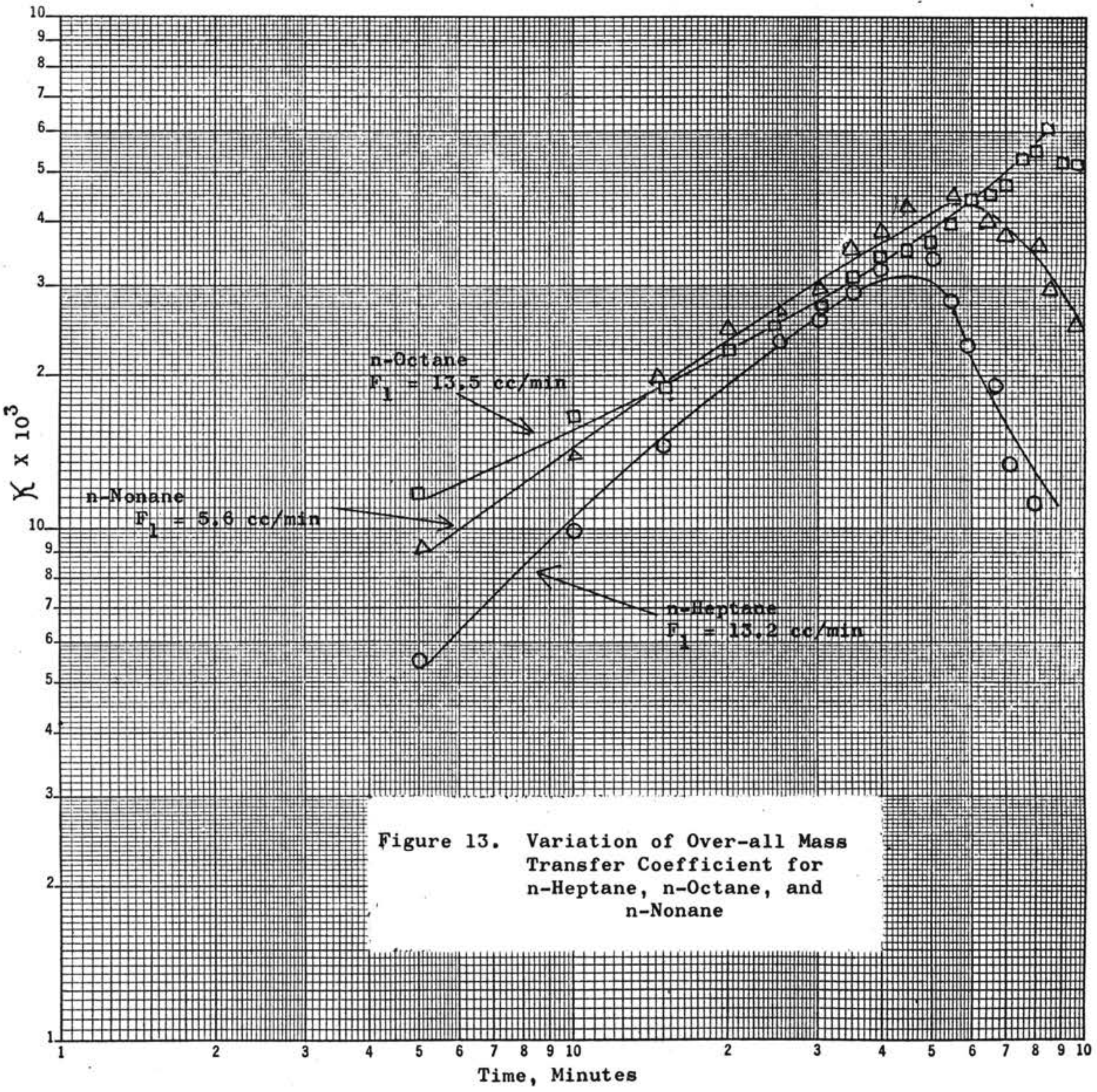


Figure 13. Variation of Over-all Mass Transfer Coefficient for n-Heptane, n-Octane, and n-Nonane

As can be seen from Tables VII and VIII, the difference, $(C_1 - C_o)$ is approximately equal to C_1. Therefore, equation 15 can be written as:

$$\frac{dw}{d\theta} = \rho \frac{F_1 - F_2}{V} = K_{ma} C_1 \qquad (15a)$$

Equation 15a was used to estimate the value of K_{ma}, the mass transfer coefficient. During the constant rate period, as is apparent from the above equation, K_{ma} is constant. Figures 15, 16 and 17 are the graphs of K_{ma} versus time for heptane, octane and nonane, respectively.

Unfortunately, these results do not prove that the mechanism is one of mass transfer. They are of primary value in design calculations. Further work is necessary to determine the actual rate controlling mechanism.

TABLE VI

EQUILIBRIUM CONCENTRATION OF OCTANE IN URBA SOLUTION AT 27.1° C

Weight Per Cent Urea	$\frac{\text{cc. Octane}}{\text{100 cc. soln.}} \times 10^5$	Volume Per Cent Isobutyl Alcohol
10	12.2	5
20	5.40	5
30	3.78	5
40	2.84	5
50	2.73	5

TABLE VII

SOLUBILITY OF N-PARAFFIN HYDROCARBONS IN WATER-ADDITIVES SOLUTIONS

AT 27.10° C

Volume Per Cent Isobutanol	n-Heptane mole/l.	n-Octane mole/l.	n-Nonane mole/l.	n-Decane mole/l.	Volume Per Cent Acitic Acid
4	2.22×10^{-3}	1.21×10^{-3}	3.85×10^{-4}	1.96×10^{-4}	1
5	2.68×10^{-3}	1.40×10^{-3}	5.50×10^{-4}	2.68×10^{-4}	1
6	3.14×10^{-3}	1.63×10^{-3}	6.60×10^{-4}	3.37×10^{-4}	1
7	3.55×10^{-3}	1.81×10^{-3}	7.70×10^{-4}	4.04×10^{-4}	1
8		2.01×10^{-3}	8.80×10^{-4}	4.71×10^{-4}	1

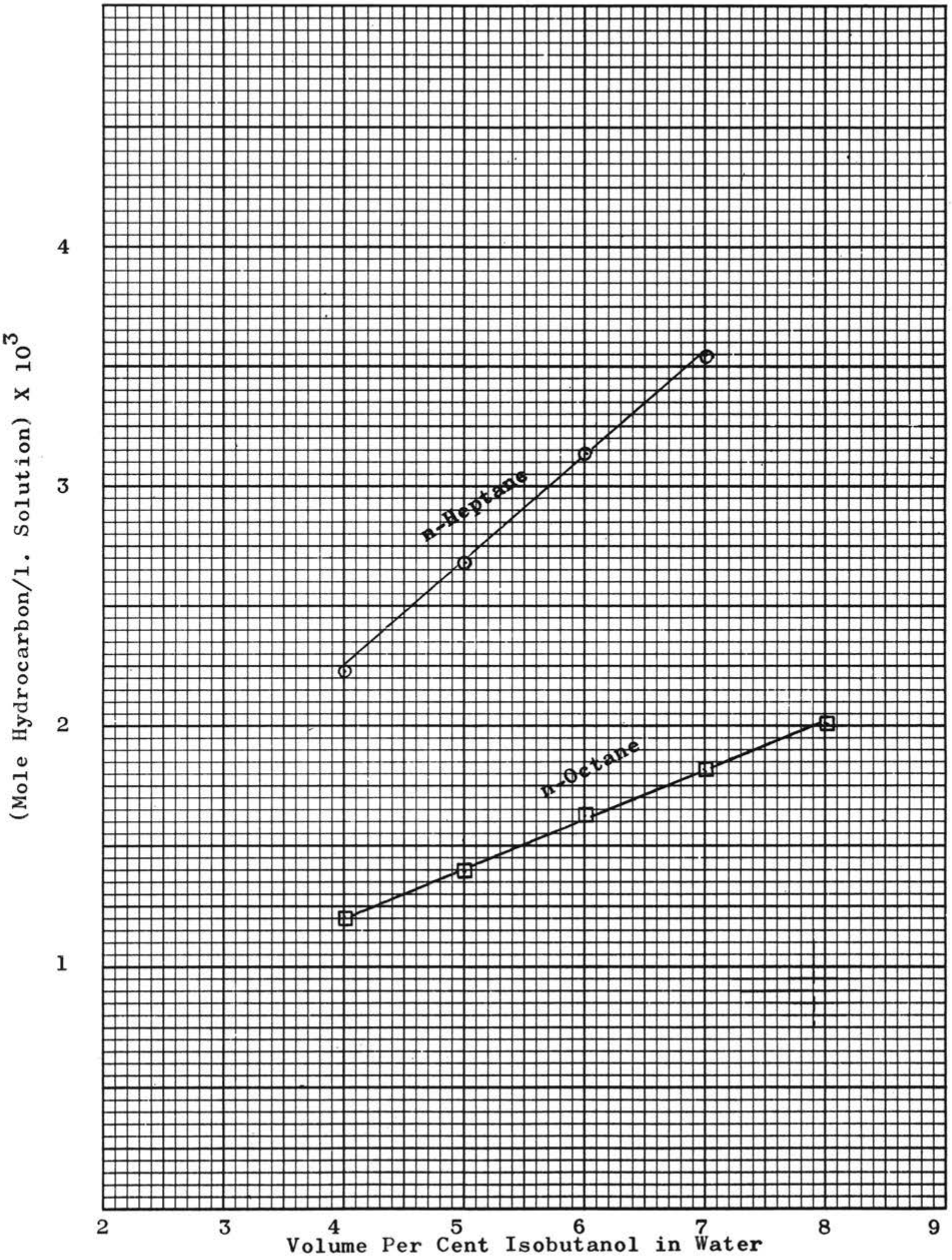


Figure 14. Solubility of n-Heptane and n-Octane in Water Containing One Per Cent Acidic Acid and Varying Amounts of Isobutanol

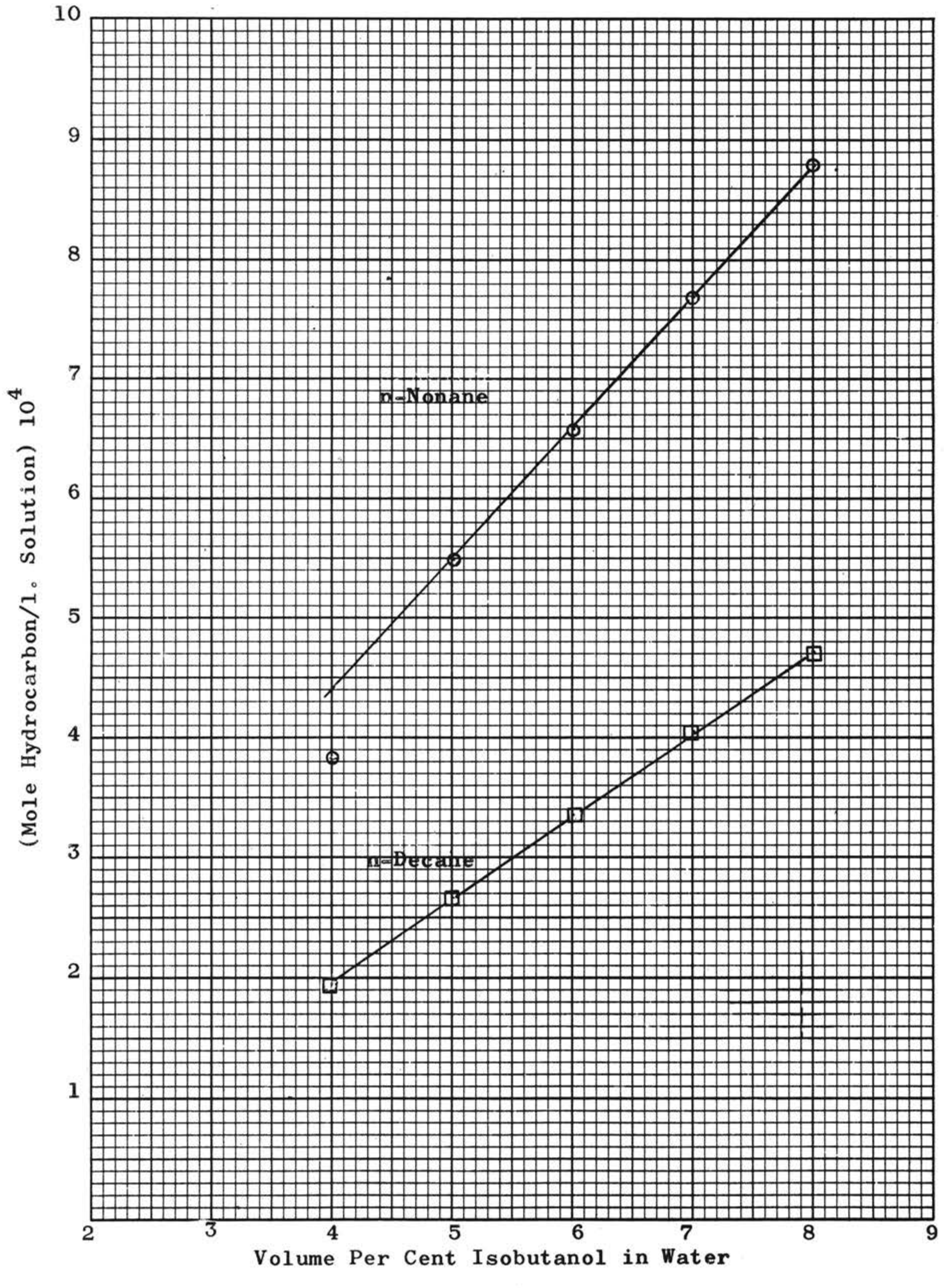


Figure 15. Solubility of n-Nonane and n-Decane in Water Containing One Per Cent Acetic Acid and Varying Amounts of Isobutanol

TABLE VIII

SOLUBILITY OF N-PARAFFIN HYDROCARBONS IN ISOBUTANOL SOLUTIONS

AT 27.10° C

Volume Per Cent Isobutanol	n-Heptane mole/l.	N-Octane mole/l.	n-Nonane mole/l	n-Decane mole/l.	Volume Per Cent Acetic Acid
4.0	7.25×10^{-4}	3.11×10^{-4}	1.77×10^{-4}	1.52×10^{-4}	0.0
5.0	7.79×10^{-4}	3.40×10^{-4}	1.98×10^{-4}	1.67×10^{-4}	0.0
6.0	8.58×10^{-4}	3.80×10^{-4}	2.20×10^{-4}	1.86×10^{-4}	0.0
7.0	9.27×10^{-4}	4.10×10^{-4}	2.53×10^{-4}	2.02×10^{-4}	0.0

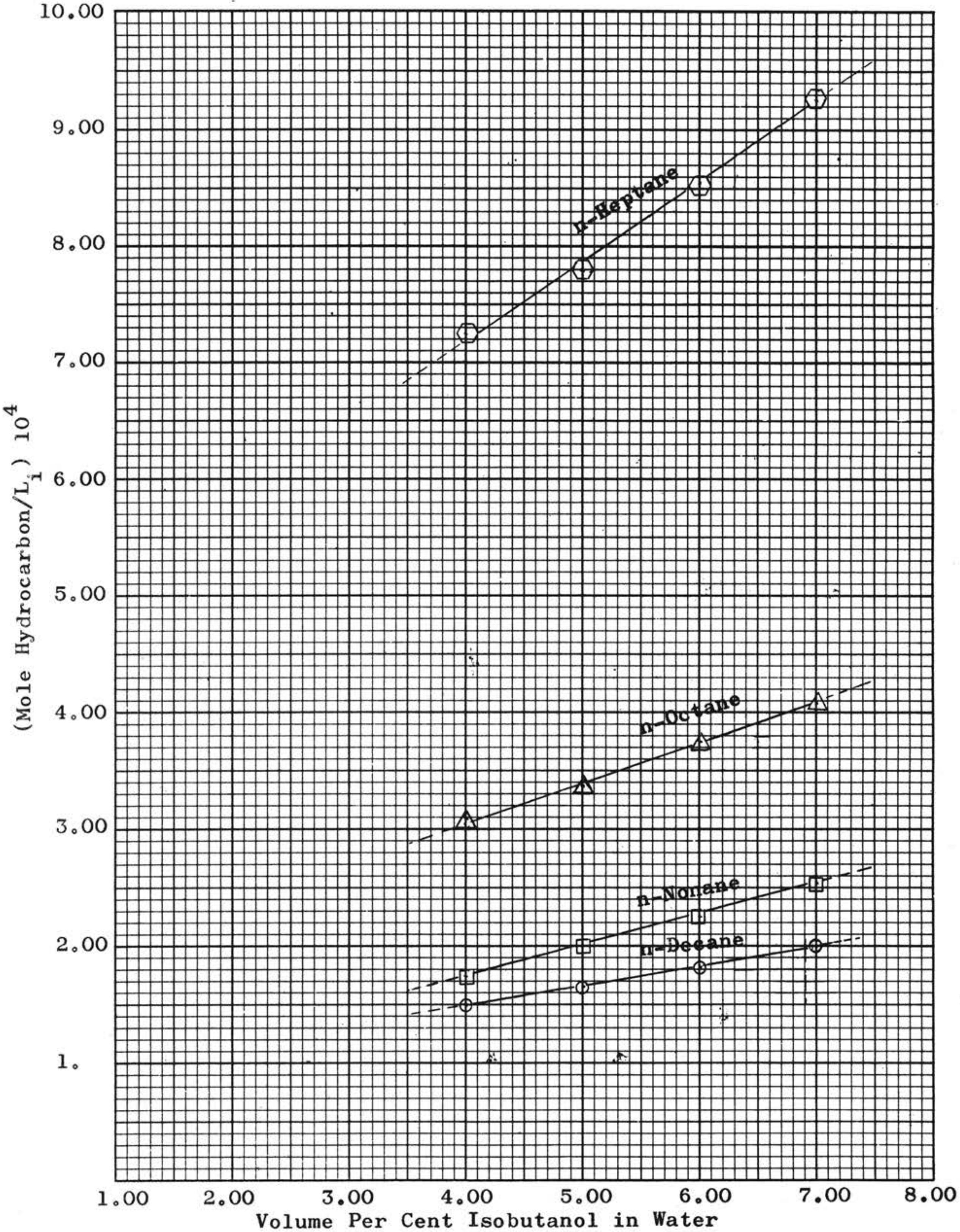


Figure 16. Solubility of n-Heptane, n-Octane, n-Nonane and n-Decane in Isobutanol-Water Solution Varying the Amounts of Isobutanol

TABLE IX

MASS TRANSFER COEFFICIENT FOR OCTANE AVERAGE INLET FLOW RATE 13.5 AT TEMPERATURE 25° C

Time Min.	F_1 cc/min.	F_2 cc/min.	L Cm	V cc	$F_1 - F_2$	$\frac{\rho (F_1 - F_2) 10^3}{V}$	$C_1 \times 10^3$	K_{ma}
5	13.60	13.10	32.2	300	0.50	1.17	1.40	0.836
10	12.81	12.00	32.2	300	0.81	1.89	1.40	1.35
15	13.80	12.80	32.0	297	1.00	2.33	1.40	1.67
20	13.75	12.81	32.0	297	0.94	2.20	1.40	1.57
25	13.60	12.61	32.0	297	0.99	2.34	1.40	1.67
30	13.60	12.58	32.1	299	1.02	2.38	1.40	1.70
35	13.60	12.58	32.1	299	1.02	2.38	1.40	1.70
40	13.60	12.56	32.1	299	1.04	2.42	1.40	1.73
45	13.80	12.80	32.1	299	1.00	2.33	1.40	1.67
50	14.10	13.08	32.2	300	1.02	2.38	1.40	1.70
55	14.00	13.10	32.2	300	0.90	2.10	1.40	1.50
60	14.10	13.15	32.2	300	0.85	1.91	1.40	1.37
65	13.20	12.40	32.2	300	0.80	1.87	1.40	1.34
70	13.20	12.60	32.2	300	0.60	1.40	1.40	1.00
75	13.20	12.60	32.2	300	0.60	1.40	1.40	1.00
80	12.80	12.30	32.2	300	0.50	1.17	1.40	0.836
85	12.80	12.35	32.2	300	0.45	1.05	1.40	0.750
90	12.80	12.40	32.2	300	0.40	0.93	1.40	0.664

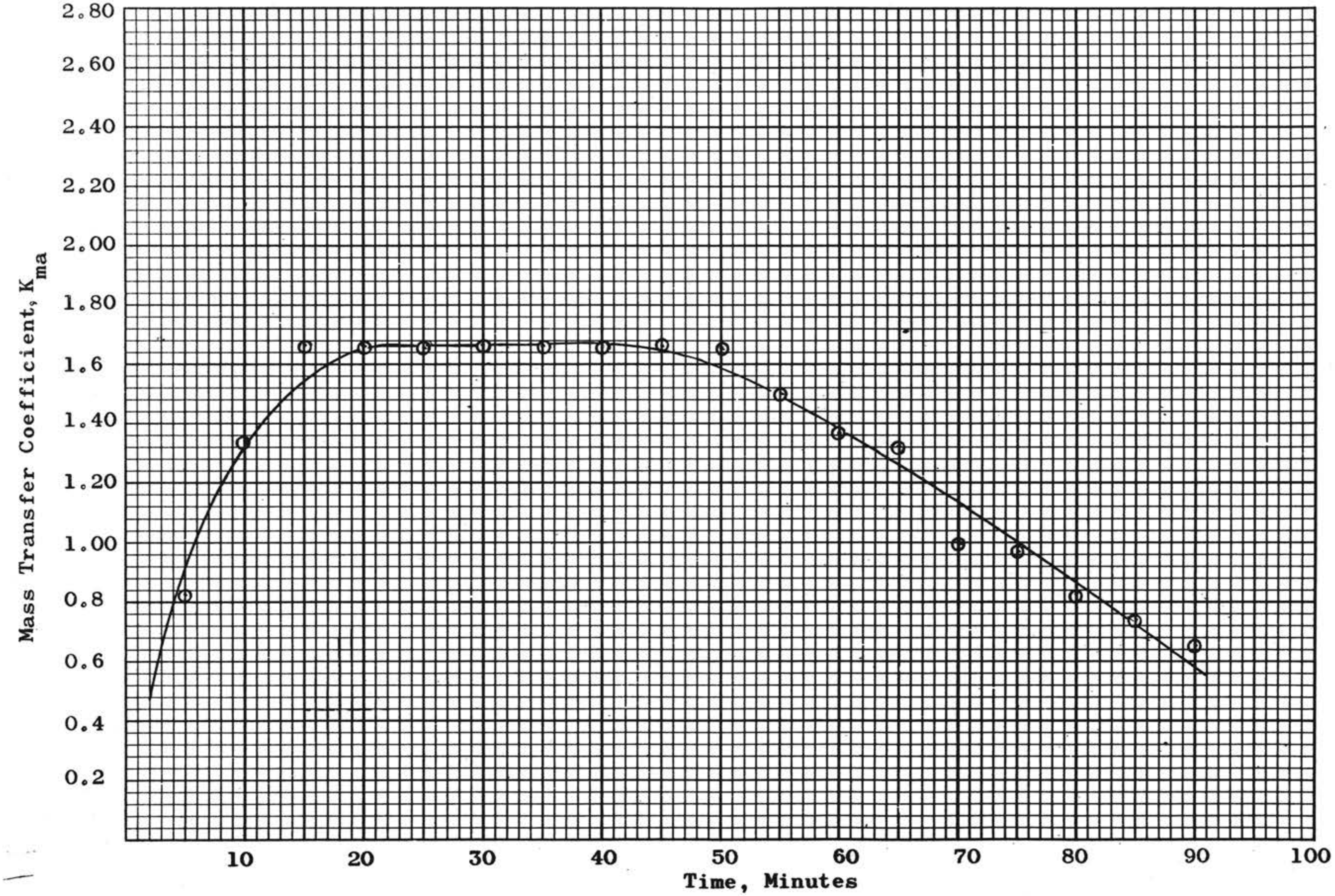


Figure 17. Variation of n-Octane Mass Transfer Coefficient with Time, F_1 = 13.5 cc/min.

TABLE X

MASS TRANSFER COEFFICIENT FOR N-OCTANE AVERAGE INLET

FLOW RATE = 3.95 AT TEMPERATURE 25° C

Time Min.	F_1 cc/min.	F_2 cc/min.	L Cm	V cc	$F_1 - F_2$	$\frac{\rho (F_1 - F_2) 10^3}{V}$	$C_1 \times 10^3$	K_{ma}
5	3.80	3.50	32.5	300	0.30	0.70	1.40	0.500
10	3.80	3.35	32.5	300	0.45	1.05	1.40	0.750
15	3.95	3.35	32.6	300	0.60	1.50	1.40	1.07
20	3.95	3.20	32.6	302	0.75	1.74	1.40	1.24
25	3.95	3.10	32.6	302	0.85	1.96	1.40	1.400
30	3.95	3.03	32.6	302	0.92	2.13	1.40	1.520
35	3.95	3.00	32.7	304	0.95	2.18	1.40	1.560
40	3.95	3.00	32.7	304	0.95	2.18	1.40	1.560
45	3.95	3.00	32.7	304	0.95	2.18	1.40	1.560
50	3.95	3.01	32.6	302	0.94	2.18	1.40	1.560
55	3.95	3.0	32.6	302	0.95	2.18	1.40	1.560
60	3.95	3.01	32.6	302	0.94	2.17	1.40	1.560
65	3.95	3.10	32.7	304	0.85	1.96	1.40	1.400
70	3.95	3.20	32.6	302	0.75	1.74	1.40	1.240
75	3.95	3.30	32.6	302	0.60	1.38	1.40	0.985
80	3.95	3.45	32.6	302	0.50	1.16	1.40	0.829
85	3.95	3.50	32.6	302	0.45	1.04	1.40	0.743
90	3.95	3.60	32.6	302	0.35	0.81	1.40	0.579
95	3.95	3.67	32.6	302	0.28	0.65	1.40	0.466
100	3.95	3.73	32.6	302	0.20	0.47	1.40	0.339
105	3.95	3.73	32.6	302	0.20	0.47	1.40	0.339

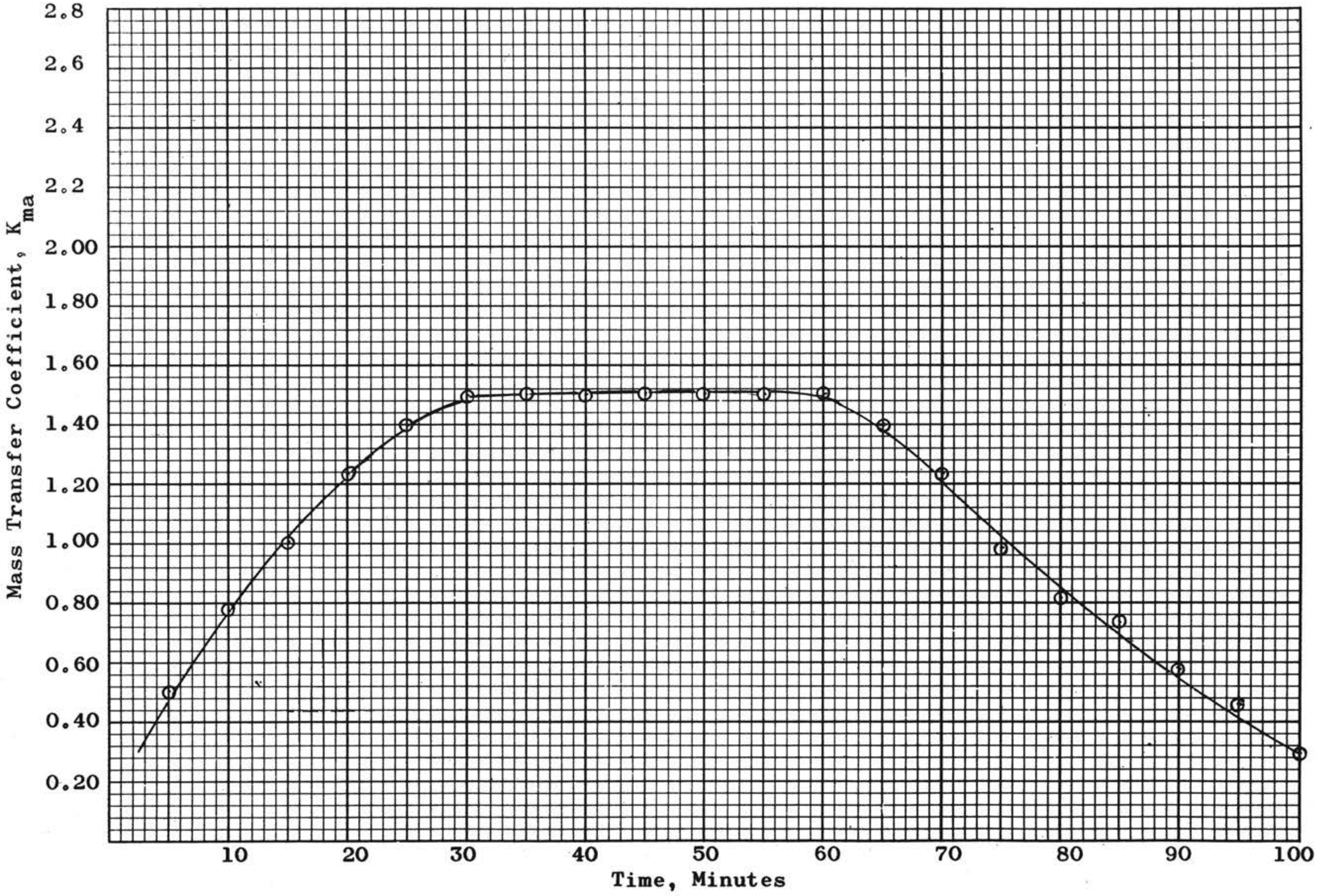


Figure 18. Variation of n-Octane Mass Transfer Coefficient with Time, F_1 = 3.95 cc/min.

TABLE XI

MASS TRANSFER COEFFICIENT FOR HEPTANE AVERAGE INLET

FLOW RATE 13.2 at 25° C

Time Min.	F_1 cc/min.	F_2 cc/min.	L Cm	V cc	$F_1 - F_2$	$\frac{\rho (F_1 - F_2) 10^3}{V}$	$C_1 \times 10^3$	K_{ma}
5	13.95	13.65	32.0	300	0.30	0.680	2.68	0.254
10	14.00	13.50	32.0	300	0.50	1.13	2.68	0.423
15	12.80	12.10	32.0	300	0.70	1.59	2.68	0.594
20	12.80	11.82	32.0	300	0.98	2.20	2.68	0.822
25	13.00	12.00	31.8	297	1.00	2.28	2.68	0.851
30	12.10	11.10	31.8	297	1.00	2.28	2.68	0.851
35	12.10	11.10	31.8	297	1.00	2.28	2.68	0.851
40	12.30	11.30	32.0	300	1.00	2.27	2.68	0.851
45	12.20	11.21	32.0	300	0.99	2.78	2.68	0.851
50	11.98	11.12	32.0	300	0.86	1.95	2.68	0.728
55	12.60	11.95	32.0	300	0.65	1.47	2.68	0.550
60	12.30	11.80	32.0	300	0.50	1.13	2.68	0.422
65	14.16	13.70	32.0	300	0.40	0.905	2.68	0.337
70	14.50	14.24	32.0	300	0.26	0.592	2.68	0.221
75	14.50	14.28	32.0	300	0.22	0.50	2.68	0.187
80	14.06	13.86	32.0	300	0.20	0.47	2.68	0.178
85	14.00	13.80	32.0	300	0.20	0.47	2.68	0.178

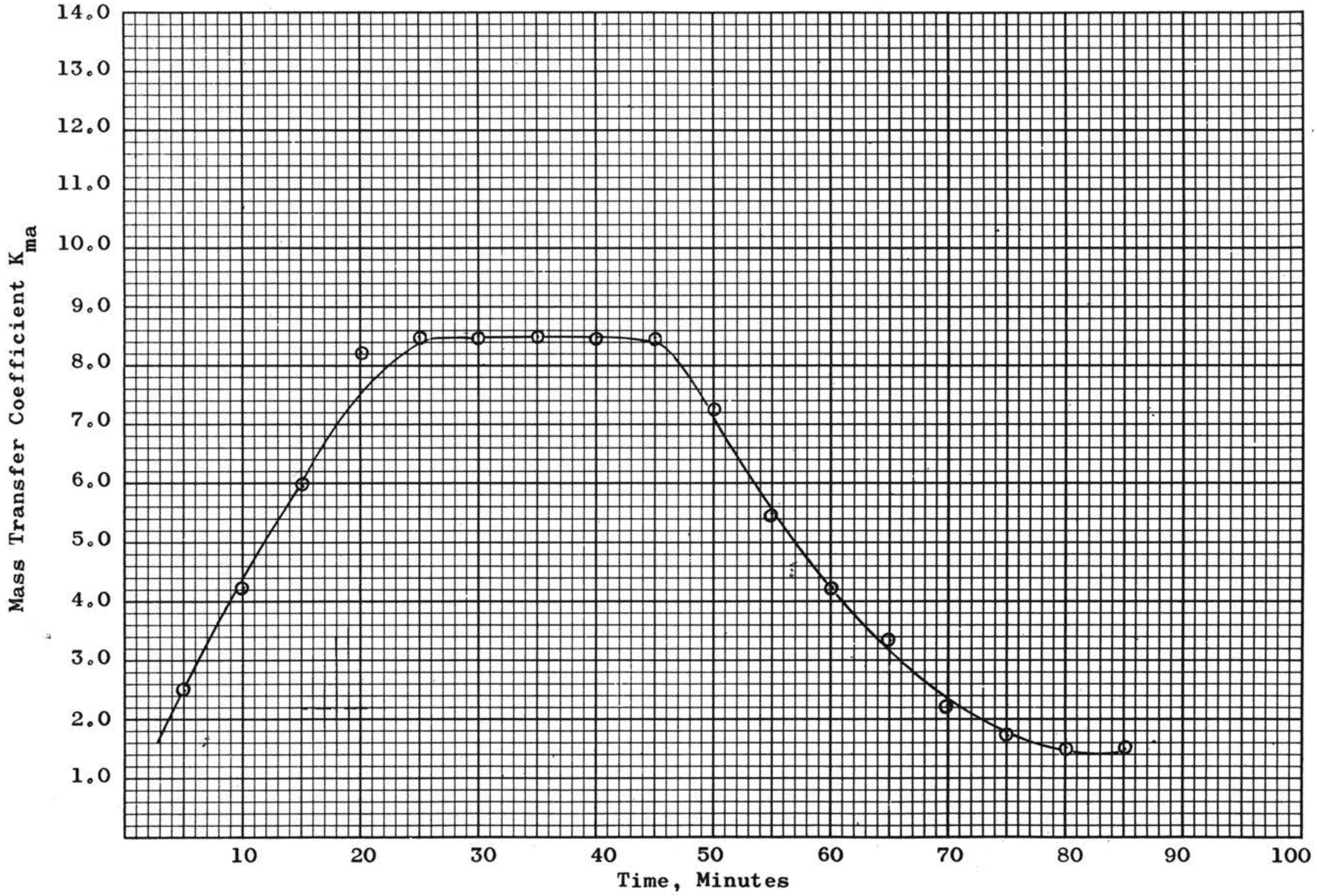


Figure 19. Variation of n-Heptane Mass Transfer Coefficient with Time, F_1 = 13.2 cc/Min.

TABLE XII

MASS TRANSFER COEFFICIENT FOR n-OCTANE AVERAGE

INLET FLOW RATE 19.80 AT TEMPERATURE OF 25° C

Time Min.	F_1 cc/min.	F_2 cc/min.	L Cm	V cc	$F_1 - F_2$	$\frac{\rho (F_1 - F_2) 10^3}{V}$	$C_1 \times 10^3$	K_{ma}
5.00	18.5	18.00	33.0	300	0.50	1.17	1.40	0.836
10.00	27.32	25.3	33.4	305	0.80	1.83	1.40	1.30
15.00	20.25	19.45	33.4	305	0.80	1.83	1.40	1.30
20.00	19.80	18.73	33.4	305	1.07	2.46	1.40	1.76
25.00	19.80	18.70	33.4	305	1.10	2.52	1.40	1.80
30.00	19.80	18.70	33.4	305	1.10	2.52	1.40	1.80
35.00	19.80	18.70	33.4	305	1.07	2.47	1.40	1.77
40.00	19.80	18.71	33.4	305	1.09	2.50	1.40	1.80
45.00	19.80	18.70	33.4	305	1.10	2.52	1.40	1.80
50.00	19.80	18.90	33.4	305	0.90	2.06	1.40	1.47
55.00	19.80	18.95	33.4	305	0.85	1.95	1.40	1.39
60.00	19.80	19.05	33.4	305	0.75	1.72	1.40	1.23
65.00	19.80	19.20	33.4	305	0.60	1.38	1.40	0.985
70.00	19.80	19.30	33.4	305	0.50	1.15	1.40	0.823
75.00	19.80	19.30	33.4	305	0.50	1.15	1.40	0.923
80.00	19.80	19.45	33.4	305	0.35	0.805	1.40	0.575
85.00	19.80	19.55	33.4	305	0.25	0.582	1.40	0.416
90.00	19.80	19.60	33.4	305	0.20	0.460	1.40	0.329
95.00	19.80	19.60	33.4	305	0.20	0.460	1.40	0.329

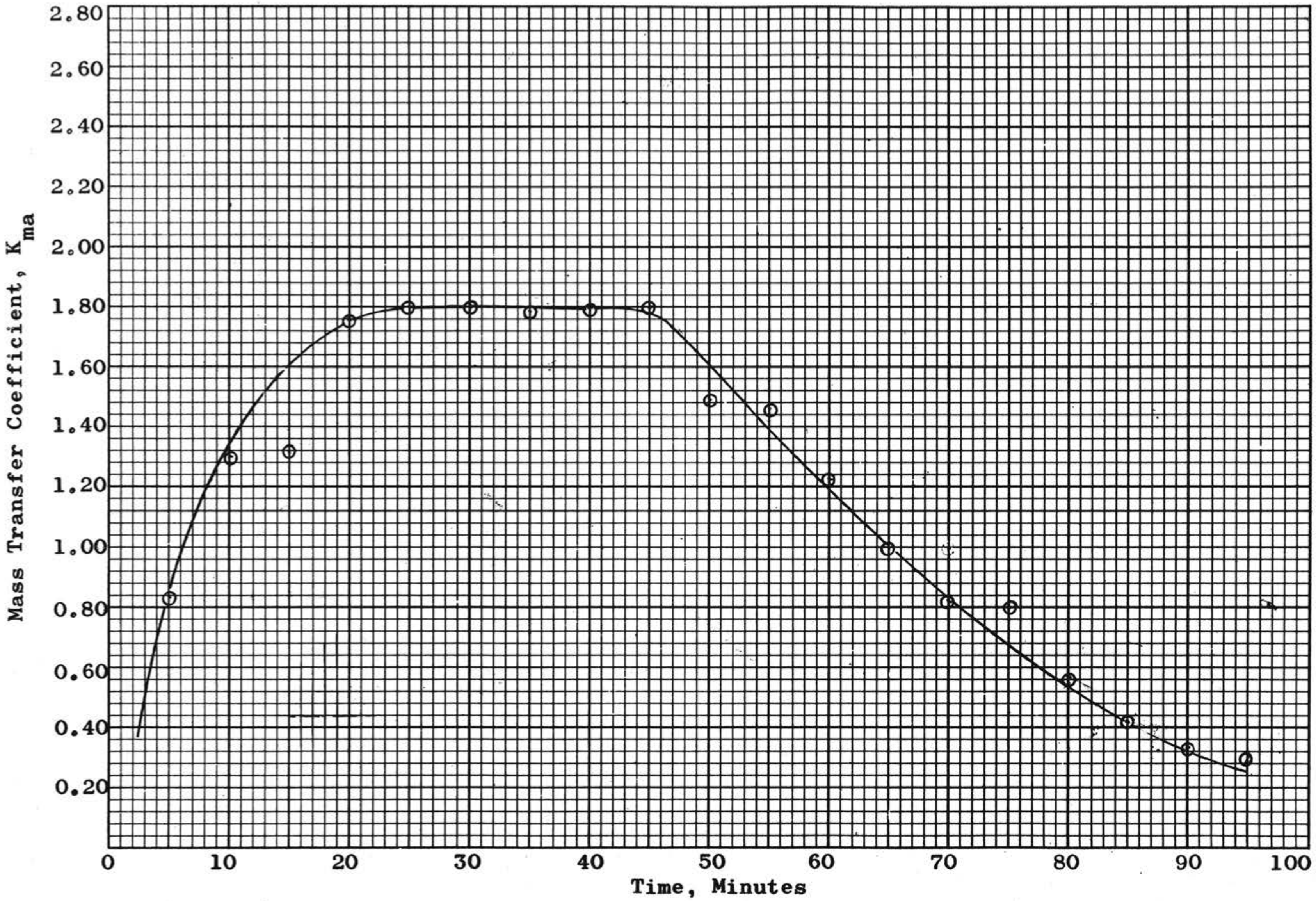


Figure 20. Variation of n-Octane Mass Transfer Coefficient with Time, F_1 = 19.8 cc/Min.

TABLE XIII

MASS TRANSFER COEFFICIENT FOR NONANE AVERAGE INLET FLOW RATE

5.60

Time Min.	F_1 cc/min.	F_2 cc/min.	L Cm	V cc	$F_1 - F_2$	$\frac{\rho\,(F_1 - F_2)\,10^3}{V}$	$C_1 \times 10^3$	K_{ma}
5	6.10	5.42	30.8	300	0.68	1.61	0.66	2.44
10	5.90	5.00	30.8	300	0.90	2.14	0.66	3.24
15	5.80	4.60	30.8	300	1.20	2.85	0.66	4.32
20	5.65	4.60	30.8	300	1.05	2.50	0.66	3.79
25	5.65	4.60	30.8	300	1.05	2.50	0.66	3.79
30	5.65	4.60	30.8	300	1.05	2.50	0.66	3.79
35	5.65	4.60	30.8	300	1.05	2.50	0.66	3.79
40	5.55	4.50	30.8	300	1.05	2.50	0.66	3.70
45	5.55	4.55	30.8	300	1.06	2.38	0.66	3.61
50	5.55	4.63	30.8	300	0.92	2.19	0.66	3.32
55	5.55	4.66	30.9	302	0.89	2.10	0.66	3.18
60	5.55	4.68	31.0	303	0.87	2.05	0.66	3.11
65	5.55	4.73	31.0	303	0.82	1.93	0.66	2.93
70	5.55	4.80	31.0	303	0.75	1.76	0.66	2.67
75	5.55	4.82	31.0	303	0.73	1.71	0.66	2.54
80	5.55	4.85	31.0	303	0.70	1.65	0.66	2.50
85	5.55	4.81	31.0	303	0.74	1.70	0.66	2.58
90	5.50	5.00	31.0	303	0.50	1.18	0.66	1.79
95	5.30	4.90	31.0	303	0.40	0.94	0.66	1.42
100	5.30	4.95	31.0	303	0.35	0.822	0.66	1.26

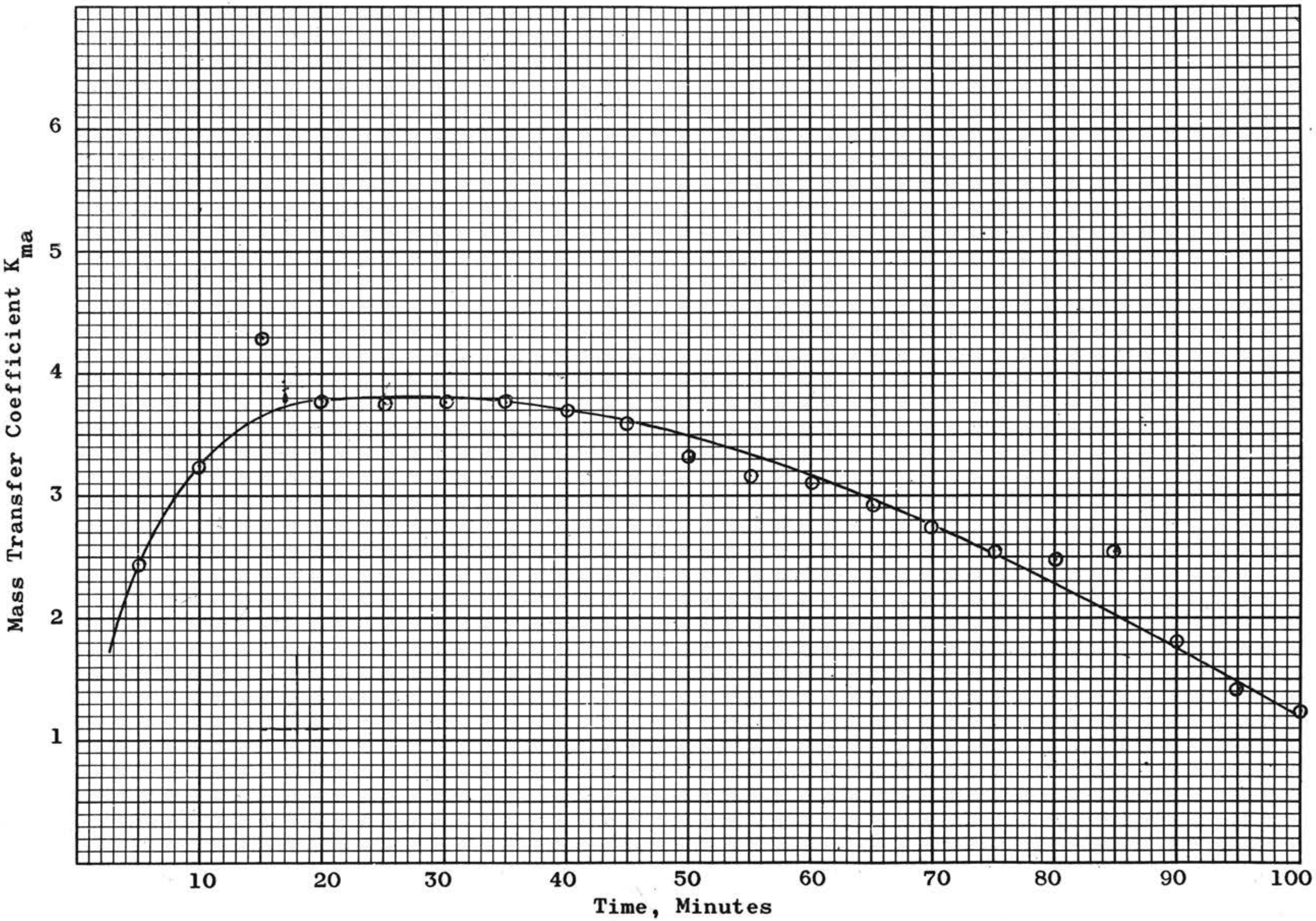


Figure 21. Variation of n-Nonane Mass Transfer Coefficient with Time, F_1 = 5.60 cc/Min.

CHAPTER V

RESULTS AND DISCUSSION

In determination of the solubility of the n-paraffin hydrocarbons, the hydrocarbon was added to a water, additives solution and the solution was stirred at room temperature. It was placed, then, in a constant temperature bath. The room temperature, however, was less or around the bath temperature, 27.1° C. Therefore, since the solubility of hydrocarbons is directly proportional to the temperature, the error introduced by this method was not a serious one. Another error that can be attributed to the variation in temperature during each run is as follows. In order to perform the saturation test on the solution, it had to be taken out of the constant temperature bath. Since the room temperature was lower than the bath temperature, had the solution been slightly below the saturation point at the bath temperature, the test might have been positive. Despite the above disadvantages of this technique, the results obtained were consistent.

The major error in determination of the solubility of hydrocarbons could have been due to an error in measurement of the amount of hydrocarbon added to the solution. The solubility of n-paraffins in water is very low, of the order of 0.001 cc. per 100 cc. of solution. A small error in volume of hydrocarbon added, would cause a large error in the solubility data. This error was minimized by taking a relatively large volume of solution, about 500 to 700 cc. The hydrocarbon was measured with one 10 λ syringe graduated to 0.2 of a λ.

Determination of Solubility of Urea in Water-Additives Solution

Due to the basic properties of urea, the solubility of urea in water is relatively high (approximately 50 grams per 100 grams of solution). Therefore, an error of 0.001 grams in weighing the urea sample, would cause only 0.002 per cent error in results. Considering this fact, the weight of urea was measured accurately to 0.001 grams.

The major error in determination of the solubility of urea was due to the hydrolysis of urea in basic or acidic solutions. The hydrolysis of urea was found to be negligible in the presence of isobutanol alone. When acetic acid was present the effect of hydrolysis was more severe, especially when the concentration of isobutanol was less than four per cent. The extrapolated value of urea dissolved in zero per cent isobutanol (Figure 22) and one per cent acetic acid is much higher than the value without acetic acid. A part of this difference is caused by hydrolysis of urea in the presence of acetic acid. As the percentage of isobutanol increases the effect of hydrolysis decreases. This can be attributed to the reaction between acetic acid and isobutanol.

TABLE XIV

SOLUBILITY OF UREA IN WATER PLUS ADDITIVES AT 27.1° C.

Volume Per Cent Isobutyl Alcohol	One Per Cent Acetic Acid		Without Acetic Acid	
	Weight of Urea 100 cc. Solvent	Weight Per Cent Urea	Weight of Urea 100 cc. Solvent	Weight Per Cent Urea
7	107.4	52.25	101.2	50.06
6	115.9	54.00	105.0	51.6
5	123.2	55.49	109.0	52.43
4	130.2	56.88	113.2	53.40
3	138.8	58.24	.....	.....
0	.....	.....	.....	55.9

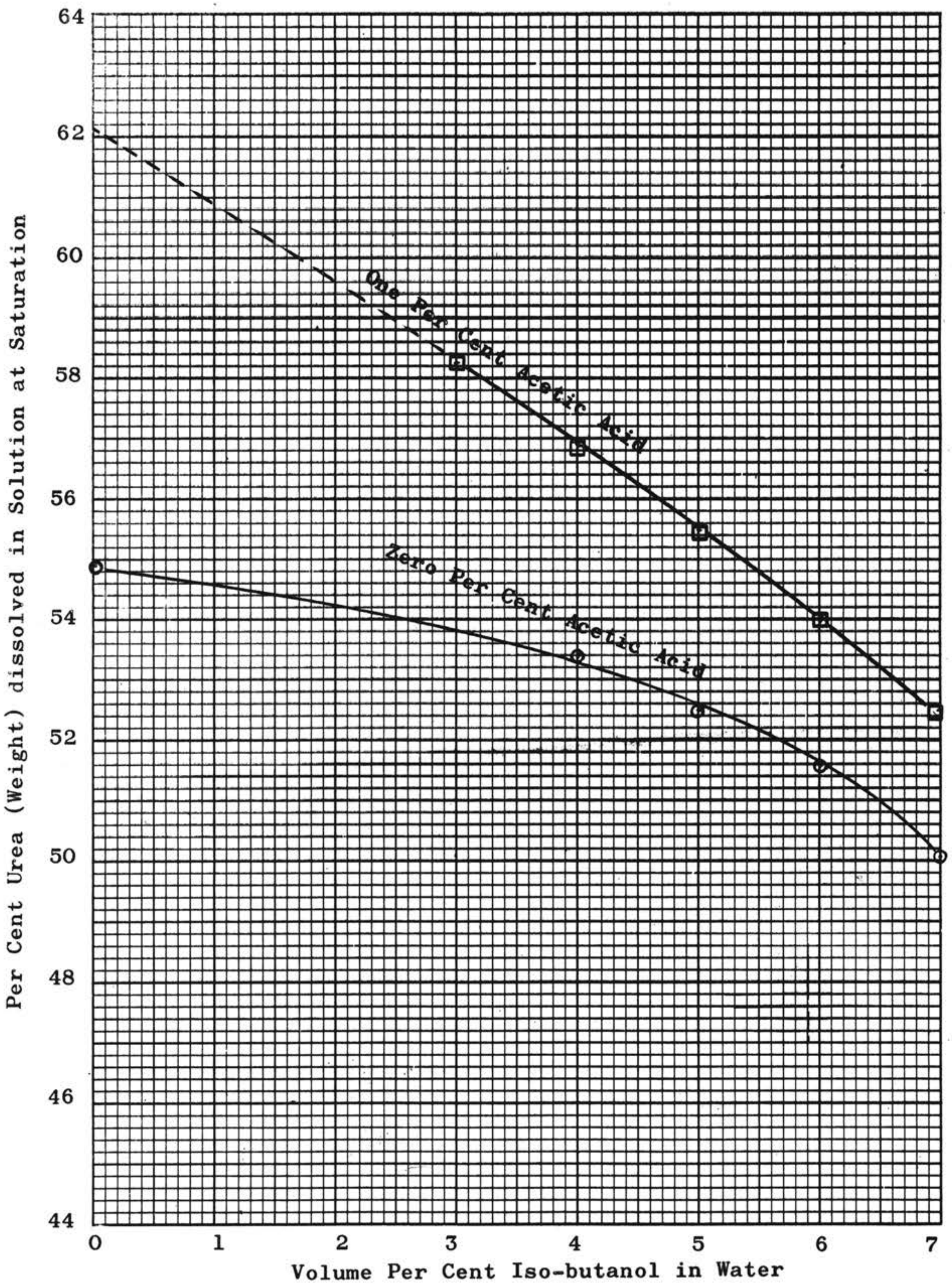


Figure 22. Solubility of Urea in Water Containing Acetic Acid and Varying Amounts of Isobutanol.

Over-all Coefficient

In determination of the rate of absorption of straight chain hydrocarbons by urea solution, using a packed column, the following cycle was observed. The rate increased, stayed constant for a period of time, and then decreased with respect to time.

As the hydrocarbon traveled through the packed column, more hydrocarbon molecules were exposed to the urea molecules. The time required for the first hydrocarbon molecules to reach the top of the column was less than two minutes. Consequently, the area of contact was fairly constant after two minutes. But the constant rate did not start before 15 minutes after the experiment was started. Therefore, the contact area was not the only factor which caused an increasing rate in the beginning of the experiment. The reaction between urea and straight chain saturated hydrocarbons is not a simultaneous reaction. The organic molecules must be in contact with urea molecules for some time before they could be absorbed. This phenomenon must be another factor causing an increase in the rate of absorption for the first fifteen minutes of the experiment. A longer column may help to determine which one of these two factors is of primary importance.

The constant period observed in the experiment indicated that a dynamic equilibrium was reached in the column and it was dominating until most of the urea molecules in the column were saturated with the hydrocarbon molecules. Again, as in the beginning of the experiment, the urea molecules located in the bottom of the column were in contact with more hydrocarbon molecules than those in the upper part of the column. Consequently, the saturation of the urea molecules started from the bottom of the column.

In future investigations, it would be of great interest if saturated urea solution is passed downward through a packed column containing n-paraffin hydrocarbon. The solubility of urea complexes formed is lower in hydrocarbons than water. In fact, water will break up the urea complexes. As a result, the rate of urea crystallization is higher when they are crystallized from hydrocarbon solution than from water-urea solution. Furthermore, if urea solution is supplied to hydrocarbon, the abundance of urea molecules will cause a faster reaction. One mole of urea, for instance, will absorb less than 0.17 mole of octane (equation 11). Therefore, having a fixed volume of octane and forcing a large amount of urea solution through it, results in more effective absorption. This phase of investigation could not be carried out with the present equipment, but more emphasis should be put on it in future investigations.

Mass Transfer Coefficient, K_{ma}, and Mechanism

The mass transfer coefficient determined by equation 15a serves to bring out several aspects of urea adduction. Experimental values of K_{ma} are presented in Tables IX through XIII. The constant rate values of K_{ma} for the three octane runs, Tables IX, X and XII, show the average of:

$K_{ma} = 1.56$ for $F_1 = 2.95$ cc/min.
$K_{ma} = 1.70$ for $F_1 = 13.5$ cc/min.
$K_{ma} = 1.8$ for $F_1 = 19.8$ cc/min.

This general increase of K_{ma} with flow rate is consistent with experimental mass transfer results in other areas.

For the three hydrocarbons studied, the average constant rate values of K_{ma} are:

n-heptane: $K_{ma} = 0.85$ for $F_1 = 13.2$
n-octane: $K_{ma} = 1.70$ for $F_1 = 13.5$
n-nonane: $K_{ma} = 3.79$ for $F_1 = 5.60$

These results are somewhat different than what might be expected for a mass transfer mechanism. The Schmidt number for these three hydrocarbons diffusing through water is very nearly constant. That is, the diffusivity of n-heptane, n-octane and n-nonane in water is about the same in each case; also the density and viscosity remain essentially the same for each system. As a result, one would not expect very much difference in the mass transfer coefficient in going from one system to another if all other forces remain constant. As shown above, n-heptane and n-octane data were taken at nearly the same flow rate, but the mass transfer coefficients differ considerably. Also, since n-nonane and n-octane have about the same Schmidt number, the low flow rate data for n-nonane seem inconsistent with the n-octane data. For this case the indication is that K_{ma} increases as flow rate is decreased.

One possible explanation of this difficulty lies in the fact that the value of C_i for n-heptane is greater than

C_i for n-octane. Tables IV and VII show that during the constant rate period $(F_1 - F_2)$ for both n-heptane and n-octane was essentially the same. Also, it can be seen from equation 15a that the factor which contributes to the difference in K_{ma} for these two systems is C_i. Values of C_i from Tables VII and VIII are for n-heptane 0.00268 and for n-octane 0.0014. There is no apparent reason for concluding that these data have more than five per cent error. As a consequence, the values of K_{ma} appear to be significantly inconsistent and indicate that the controlling mechanism for adduction is probably not one of mass transfer of hydrocarbon into the aqueous solution. Another argument against a mass transfer is the relatively small increase in K_{ma} for n-octane with increased in flow rate.

At the present time, it is not possible to establish whether or not the controlling mechanism is one of the crystal growth. If the degree of supersaturation were constant when $(F_1 - F_2)$ is constant, this would lend strong support to a mechanism of this nature. Further work will have to be done to determine the degree of supersaturation.

Another technique which may serve to illustrate the adduction mechanism is to operate at different temperatures in order that energies of activation can be calculated from the experimental data. One would expect that energies of activation for crystal growth would be much larger than energies of activation for mass transfer.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Restatement of the Problem

The original purpose of this work was to determine the characteristics of the urea adducts formation. To accomplish this purpose, some preliminary data such as the solubility of n-paraffin hydrocarbons in isobutanol, acetic acid solutions had to be determined.

Conclusions

The over-all coefficient, $\mathcal{K}$, determined by equation 14, cannot directly describe any of the possible mechanisms that take place. It is, however, a design coefficient which indicates the amount of hydrocarbon absorbed by saturated urea solution at room temperature, approximately 25° C, for very specific equipment conditions.

The mass transfer coefficients obtained from equation 15a for n-octane at three different inlet flow rates are consistent with the theoretical equations and other experimental mass transfer results in other areas. The results obtained from the experiments using three different hydrocarbons; heptane, octane, and nonane, indicate that the controlling mechanism for urea adduction is probably not the mass transfer from the hydrocarbon phase to the aqueous phase.

Recommendations

Future Studies

There exists a possibility that the amount of urea present in the solution is one of the controlling factors of the rate of adduction. To investigate this matter, it is recommended that saturated urea solution is passed downward through the hydrocarbon phase in a packed column.

Equipment Alteration

Determination of the energy of activation of crystal growth is the primary factor in study of the mass transfer from the bulk liquid to the crystals. A new packed column with a glass jacket should be designed so that water from a constant temperature bath can be circulated around the column. By changing the temperature of the bath, the mass transfer coefficient and the energy of activation may be obtained at different temperatures.

Urea adduction can be studied using an agitated vessel, if the urea solution is saturated at a relatively high temperature (150° to 170° F.), but the reactor is kept at a temperature about 90° to 100° F.

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APPENDIX A

DEFINITION OF TERMS

A - interfacial area

C_1 - solubility of hydrocarbon in solution of water and additives

C_a - interfacial concentration

C_b - amount by weight of hydrocarbon absorbed by a unit volume of saturated urea solution at any given time

C_i - the maximum amount by weight of hydrocarbon that can be absorbed by a unit volume of staurated urea solution

C^* - equilibrium weight concentration of hydrocarbon in saturated urea solution.

D - molecular diffusivity

E - activation energy, energy/mole

F_1 - inlet flow rate to the column

F_2 - outlet flow rate from the column

H - heat of formation of the urea adducts, energy/mole

J - nucleation rate, number of nuclei formed per unit volume

K - mass transfer coefficient

K_{ma} - hydrocarbon-urea solution mass transfer coefficient

K_θ - equilibrium constant

k - Boltzman constant

$\mathcal{K}$ - over-all coefficient

l - diameter of mixing tank

m - mole urea/mole hydrocarbon

n - number of carbon atoms in n-paraffin hydrocarbon

N - a dimensionless number, or moles of urea in the column

p - density of the solution

ρ - density of pure hydrocarbons

R - universal gas constant

r - rate of mixing

S - fractional rate of surface renewal

T - absolute temperature

θ - time

u - viscosity of the solution

V - volume of the urea solution in the packed column

v - volume of hydrocarbon absorbed

X - fictitious film thickness

APPENDIX B

DENSITY OF ISOBUTANOL SOLUTIONS

TABLE XV

DENSITY OF ISOBUTYL ALCOHOL SOLUTION AT 27.1° C.

Volume Per Cent Isobutyl Alcohol	Density gram/cc.
8	0.9830
7	0.9842
6	0.9862
5	0.9874
4	0.9889
3	0.9915
0	0.9965
100	0.7980

APPENDIX C

SAMPLE CALCULATIONS

SAMPLE CALCULATION

Determination of Over-all Coefficient for n-Octane,

Average Inlet Flow Rate, 13.50

Operating conditions: Same as Table IV

Density of n-Octane = 0.6985 g./cc.

Density of Saturated Urea Solution = 1.215 g./cc.

Volume of the Saturated Urea Solution in the Column = 300 cc.

Per cent Urea in Solution (Weight) = 55.5

Step 1. Determination of C_i.

$$\text{Moles Urea In Column} = \frac{(55.5\text{g. Urea})(1.215\text{g. soln.})(\text{mole Urea})(300\text{cc. soln})}{(100\text{ g. soln.})(\text{cc. soln.})(60\text{ g. Urea})}$$

$$= 3.37$$

$$\frac{\text{Mole Urea}}{\text{Mole HC}} = 0.685(n - 1) + 2.181 \qquad (11)$$

$$\frac{\text{Mole Urea}}{\text{Mole Octa.}} = 0.685(n - 1) + 2.181$$

$$= 6.866$$

$$\text{Mole n-Octane absorbed} = 3.37/6.866$$

$$= 0.486$$

$$\text{Gram n-Octane absorbed} = \frac{(\text{Mole n-Octane absorbed})(\text{g n-Octane})}{\text{Mole n-Octane}}$$

$$= 0.486 \times 114$$

$$= 55.6$$

$$C_i' = \frac{\text{g. n-Octane absorbed}}{\text{Volume of Urea Soln.}}$$

$= 55.6/300$

$= 185.5 \times 10^{-3}$

$C_i = C'_i + C^*$

C^* = equilibrium concentration of n-Octane

$C^* = 2.73 \times 10^{-5}$ Table III

$C_i = 185.5 \times 10^{-3}$

Step 2. Determination of C_b (for first five minutes).

$\frac{\text{Volume n-Octane absorbed}}{(\text{Volume of Urea Soln.})(\text{Min.})} = 1.67 \times 10^{-3}$ Table IV

Graphically integration of Fig. 7 $= 8.37 \times 10^{-3}$

C_b = grams n-Octane absorbed after five minutes

= cc. n-Octane X (g. n-Octane/ cc. n-Octane)

$= 8.32 \times 10^{-3} \times 0.6985$

$= 5.84 \times 10^{-3}$

Step 3. Determination of Over-all Coefficient.

$$= \frac{F_1 - F_2}{V} \cdot \frac{1}{C_i - C_b} \qquad (14)$$

$$= 1.67 \times 10^{-3} \cdot \frac{1}{185.5 \times 10^{-3} - 5.84 \times 10^{-3}}$$

$= 9.29 \times 10^{-3}$ cc./(Min.)(g.)

VITA

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