DIFFUSION OF SINGLE AND MULTICOMPONENT SOLUTES FROM CAPILLARIES

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ABSTRACT

The purpose of this investigation was to determine the diffusion coefficients of several single-and multi-component solutes, and to establish the relations between the diffusivity, the solute composition, and the diffusion rate. Such information pertinent to the extraction and leaching operations, can not be found in literature.

The procedure developed by Piret, Ebel, Kiang, and Armstrong (25), involving observation of the extraction rate of two-phase mixtures from straight capillaries, was adopted and verified on a known sodium chloride-water system.

In the course of the experimental work diffusion coefficients were determined for ursolic acid, palmitic acid, and tripalmitin in methyl isobutyl ketone. The results compared well with values estimated by the empirical Wilke correlation (31). Diffusion coefficients of sodium chloride, potassium sulfate, cupric sulfate pentahydrate, and sucrose in water were also determined, and found to be in agreement with the values reported by the other investigators.

To evaluate diffusion coefficients of mixed solutes from experimental data, the concept of the effective interface composition, governed by the relative diffusion rate of components in the mixture, was introduced. On this basis a straight line relation was obtained between the diffusivity and the solute composition. The relation was found to apply well to most systems tested.

To correlate diffusion coefficients with the experimental extraction rate data, introduction of a factor correcting for the deviation from Fick's Law was found to be necessary. This factor, based on the solubility of solutes, is analogous to that proposed by Arnold (1,3,) for liquid-vapor systems.

Practical value of the established relations lies in the ability to predict the diffusion coefficients and the extraction rates of solutes in liquid.

ACKNOWLEDGMENT

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INTRODUCTION

Diffusion in liquids plays an important role in many theoretical and engineering calculations involving mass transfer, such as absorption, extraction, distillation, and chemical reactions.

Although considerable attention has been given to diffusion in liquids (4,11,14,17,32), the theory has not been fully developed and understood. As a result reliable liquid diffusivities seldom can be predicted. It is often necessary to resort to experimental work in order to obtain such data.

In the extraction of soluble materials from porous solids diffusion occurs and is often rate controlling. Understanding of transfer processes from within solid particles to their surface therefore is desirable.

The influence of an inert solid upon the diffusion rate of a solute was studied extensively. Boucher, Brier, and Osburn (5) reported the extraction of soybean oil from porous clay plates to be essentially a diffusional operation, the rate of which is affected by the nature of the solid. McBain and Liu (19) observed diffusion of hydrochloric acid and sucrose through porous glass diaphragms. They found that the rate of diffusion is independent of the nature and porosity of the diaphragm. Cady and Williams (6), on the other hand, studying diffusion of urea through wood fibers, reported considerable rate decrease due to possible blocking of the cell structure. Pan and

Morris (9) evaluated the effect of cellular structure and of moisture content on the diffusion rate of peanut oil from peanuts. Katz and Osburn (13) discussed structure as a variable in the application of diffusion theory to extraction. Piret, Ebel, Kiang, and Armstrong (24,25) developed theoretical equations for a single-phase and a two-phase extraction from carrier solids of diverse complexity. They verified these relations with appropriate experimental work, and introduced the concept of a pore-shape factor to account for the variation of the diffusion rate of a solute from different solids. Peterson (23) found an expression for diffusion through a pore whose cross section varied periodically along its length in a hyperbolic fashion, from which he demonstrated how the effective diffusivity in such a pore varied with the ratio of maximum and minimum cross-sectional area. Michaels (21) made a similar study with diffusion in a pore of irregular cross section.

A single-phase diffusion of mixed solutes in liquids was studied only by a few investigators. McBain and Liu (19) observed diffusion of dextrose and hydrochloric acid mixtures in water. They concluded that due to mutual bombardment of molecules, depending on the system, diffusion rate could either be retarded or accelerated. Vinograd and McBain (29) outlined the theory of diffusion in solutions of mixed ions as an expression of the Nernst theory. Dunlop and Gosting (8) and Fujita and Gosting (10), developed mathematical relations describing a freely diffusing boundary of an aqueous solution of two salts. They verified these expressions with experimental data obtained for sodium chloride-potassium chloride-water and sodium chloride-lithium chloride-water mixtures.

In spite of its importance to the extraction of natural products, information on the diffusion of mixed solutes from a solid interface into a solution does not appear in literature. The purpose of the following investigation therefore was to study such systems, to observe diffusion of single- and multi-component solid solutes from straight capillaries, to compare their diffusion rates, and to establish quantitative relations between the diffusion coefficients and the solute composition.

THEORY OF A TWO - PHASE DIFFUSION FROM CAPILLARIES

1. Diffusion of Single - Component Solutes

Piret and co-workers (25) developed mathematical expressions describing conditions of a two-phase extraction from single, smooth capillaries. Since these conditions were used during present experimental work, a brief discussion of theory, method of derivation, and results will be given. The complete list of symbols and their explanation can be found in the appendix.

It is assumed that a straight capillary of uniform cross-sectional area and finite length is initially filled with (a)cc./cm. of solid solute and (1-a)cc./cm. of saturated solution of the solute and the solvent under consideration. One end of the capillary is brought into contact with an infinite reservoir of the solvent. As soon as contact is established between the open end of the capillary and the solvent, diffusion begins. As solute diffuses from the capillary, solvent flows into the capillary; solid solute in the solute bed dissolves and the interface between solid and solution gradually recedes into the capillary.

In the course of the extraction three distinct zones are formed in the capillary. Zone 1 is composed of the initial solute bed consisting of a solid solute occupying fraction (a) , and of a saturated solution of that solute occupying the remaining fraction (1-a) ; zone 2 is formed by the solution, the solvent of which came from the solute bed; zone 3 consists of a solution the solvent of which diffused from the infinite reservoir.

Formation of zones 2 and 3 can be visualized in the following manner (Figure 1.): when the interface between the solute and the solvent recedes a distance (b)cm. , then (ab)cc. of solid solute disappear, (1-a)(b)cc. of saturated solution of concentration C_s remain, and (ab)cc. of solvent of zero concentration, C_o, flow into the capillary. The (1-a)(b)cc. of solution become a part of zone 2, and (ab)cc. of solvent become a part of zone 3. If the extraction distance is (x_s)cm. , then zone 2, by volume balance, is $(1-a)(x_s)$cc. or $(1-a)(x_s)$cm. in length.

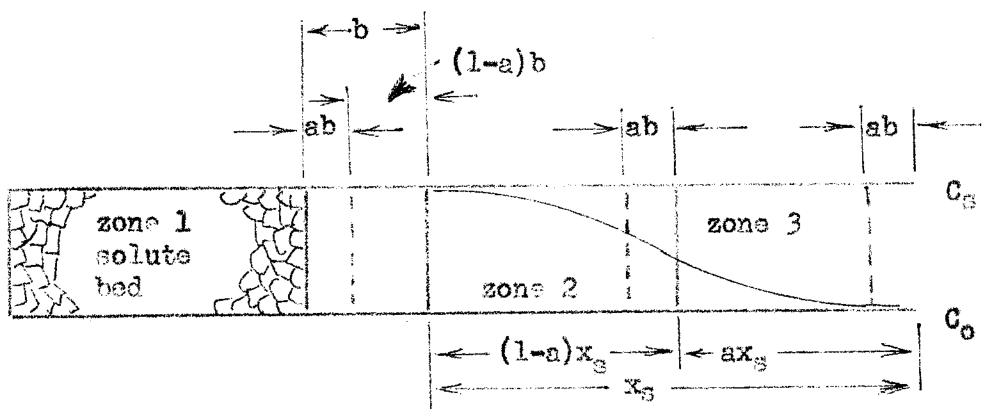


Figure 1. Formation of zones in diffusion of a two-phase solute from a capillary.

It is clear that all solvent in the diffusion path is at rest with respect to the boundary between zones 2 and 3. Fick's Second Law therefore may be written with reference to this boundary

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \tag{1}$$

where D is the diffusion coefficient defined as the proportionality factor between the rate of diffusion and the gradient of the potential causing diffusion (14). Since concentration of solute in zone 3 at any point increases with time, $\partial C/\partial t$ is a positive function. By Equation (1), $\partial^2 C/\partial x^2$ must be also a positive function, and the curve of concentration vs. distance in zone 3 is concave upward. Applying similar reasoning to zone 2, a concave downward curve of concentration vs. distance is suggested. Because $\partial^2 C/\partial x^2$ is positive in zone 3 and negative in zone 2, the point of inflection must lie on the boundary of these two zones.

The problem is to develop an equation for the rate at which the interface moves in relation to the capillary entrance. Since the solute and the solvent move in the opposite directions, the overall rate of solute leaving the interface can be expressed by the following equation.

$$N = -D \left(\frac{\partial c}{\partial x}\right)_i - vC_s \tag{2}$$

where v is the velocity of solvent at any point in the diffusion path relative to the capillary wall. N is directly related to the rate at which the interface moves. If interface moves distance x_s, and ρ_a is the apparent density of the solute bed, a quantity of solute equal to $(\rho_a - C_s)\Delta x_s$ must leave the interface.

Therefore

$$N_{av}\Delta t = (\rho_a - C_s)\Delta x_s$$

or

$$\frac{dx_s}{dt} = \frac{N}{(\rho_a - C_s)}$$

Evaluating N from Equation (2) and eliminating v by noting that the flow of solvent is equal to the product of the quantity (a) and the linear velocity of the interface, there results the expression

$$\frac{dx_s}{dt} = \frac{-D}{\rho_a - (1-a)C_s}\left(\frac{\partial C}{\partial x}\right)_i \qquad (3)$$

The solution to the stated problem must be satisfied by the following conditions:

1. The concentration of solute at the capillary entrance must be C_o for all t values larger than zero.

2. The concentration of solute at the solute-solvent interface must be C_s for all t values larger than zero.

3. A point of inflection must occur at a distance ax_s from the capillary entrance.

4. With the point of inflection at the origin of the reference frame the governing relation in the diffusion path must be Equation (1).

5. The velocity of interface recession relative to the capillary entrance and the concentration gradient at the interface must be related by Equation (3).

A general solution to the case of a single-phase, unsteady state diffusion from an initially sharp boundary in an infinite volume is expressed by the following equation found in the literature (3,29)

$$C = \frac{1}{2\sqrt{\pi Dt}} \int_{-\infty}^{\infty} f(\mu) \exp.\left[-\frac{(x-\mu)^2}{4Dt}\right] d\mu \qquad (4)$$

where $f(\mu) = C_s$ for $x < o$

and $f(\mu) = C_o$ for $x > o$

To obtain an exact solution for receding solid interface from Equation (4), two arbitrary constants are introduced, a constant N to account for high solute concentration in the solid-saturated solution mixture, and another constant s to control the position of the point of inflection. The relation of these constants to the system is shown in Fig.2. Since the diffusion path is the horizontal distance from E to F, the conditions 1 and 2 required by the solution are met. By having $f(\mu) = N+s+C_o$ for x values smaller than zero, and $f(\mu) = -N+s+C_o$ for x values larger than zero, condition 4 is also satisfied.

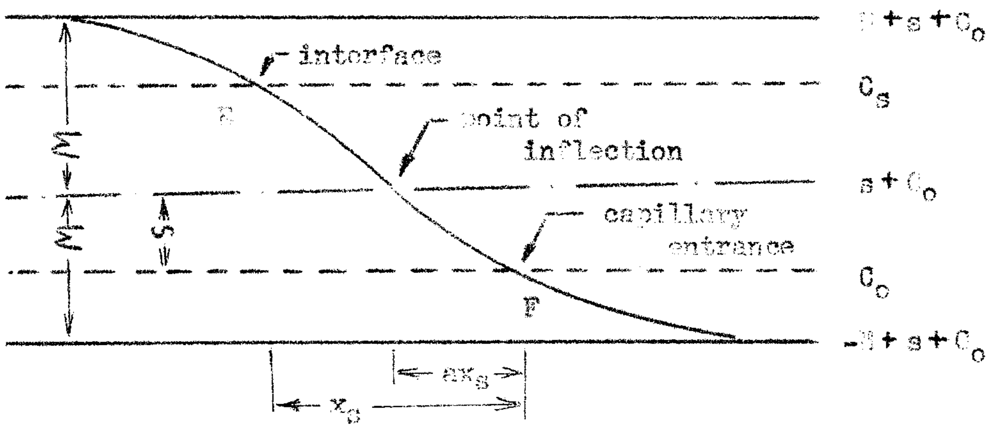


Figure 2. Adaptation of conventional solution of free diffusion in an infinite tube to the case of diffusion of a two-phase solute from a capillary.

Substitution of modified $f_i(\mu)$ values in Equation (4) and rearrangement results in

$$\frac{x}{2\sqrt{Dt}} = \Psi\left[\frac{s + C_o - C}{M}\right] \qquad (5)$$

where Ψ is an inverse of the error function

$$\frac{1}{\sqrt{\pi Dt}} = \int_0^x \exp.\left[-\frac{(x-\mu)^2}{4Dt}\right] d\mu$$

The capillary entrance is a distance ax_s from the point of inflection, and the concentration there is C_o. Equation (5) therefore becomes

$$\frac{ax_s}{2\sqrt{Dt}} = \Psi\left[\frac{s}{M}\right] \qquad (6)$$

Similary, for the solid interface, Equation (5) can be written

$$\frac{(1-a)x_s}{2\sqrt{Dt}} = \psi\left(\frac{\Delta C-s}{M}\right) \tag{7}$$

From an identity

$$\frac{ax_s}{ax_s + (1-a)x_s} = a$$

through replacement of appropriate terms from Equations (6) and (7) the following relation between a and s is obtained which satisfied condition 3 of the solution.

$$a = \frac{\psi\left(\frac{s}{M}\right)}{\psi\left(\frac{s}{M}\right) + \psi\left(\frac{\Delta C-s}{M}\right)} \tag{8}$$

The rate at which the interface moves in relation to the capillary entrance is expressed by

$$\frac{dx_s}{dt} = \frac{d(ax_s)}{dt} + \frac{d(1-a)x_s}{dt} \tag{9}$$

By taking the derivatives of Equations (6) and (7) with respect to time and substituting, the right-hand side of Equation (9) can be found

$$\frac{dx_s}{dt} = \sqrt{\frac{D}{t}}\left[\psi\left(\frac{\Delta C-s}{M}\right) + \psi\left(\frac{s}{M}\right)\right] \tag{10}$$

From Equation (4) the slope at the interface is determined

$$\left(\frac{\partial c}{\partial x}\right)_i = \frac{M}{\sqrt{\pi Dt}} \quad \exp.\left[-\frac{(1-a)^2 x_s^2}{4Dt}\right]$$

$$= -\frac{M}{\sqrt{\pi Dt}} \quad \exp.\left[-\left(\psi\frac{\Delta C-s}{M}\right)^2\right] \qquad (11)$$

Finally, using Equations (10) and (11), Equation (3) is transformed into an expression

$$\psi\left(\frac{s}{M}\right)+\psi\left(\frac{\Delta C-s}{M}\right) = \frac{M}{\sqrt{\pi}\left[\rho_s-(1-a)C_s\right]} \quad \exp.-\left[\psi\left(\frac{\Delta C-s}{M}\right)\right]^2 \qquad (12)$$

Equation (12) indicates that for any positive value of s, a value of M can be selected, satisfying thus condition 5 of the solution.

The relationship between time and distance of interface to capillary entrance, required in the evaluation of the experimental data, is obtained from Equation (6)

$$x_s = \frac{2\sqrt{Dt}}{a}\,\psi\left(\frac{s}{M}\right) \qquad (13)$$

where M and s are determined from Equations (9) and (12). Arriving at Equation (13), Mirst, Abel, Zieng, and Armstrong (25) found an expression which relates exactly the distance of recession of the solid-liquid interface to the time and the physical properties of the system.

2. Diffusion of Multi-Component Solutes.

The preceding theoretical discussion is expected to apply to any two-phase extraction from capillaries governed by free diffusion, including the extraction of multi-component solutes. To interpret experimental results obtained with such systems, however, a closer look at the mechanism of free diffusion of mixed solutes from a sharp boundary should be given.

Consider a capillary, filled initially with a uniform solid mixture of two or more solutes, and placed into a stream of flowing solvent. If free diffusion from solid-liquid boundary occurs and is rate controlling, then a sharp gradually receding interface must develop. This is possible only if the composition of solute leaving the capillary is the same as the composition of the receding solid bed. Since mobility of different molecules through a stagnant layer of a solvent is different, to insure dynamic equilibrium of the system, the developed interface must exist, the composition of which is a direct inverse of the relative diffusion rate of molecules in question.

Unidirectional diffusion rate of a solute through a stagnant solvent can be expressed by the following simple relation (3,25)

$$N = -D\left(\frac{\partial C}{\partial x}\right) \tag{14}$$

where N is the quantity of solute per unit area per unit time leaving the interface by diffusion, and $\partial C/\partial x$ is the concentration gradient of that solute in the direction of diffusion. Due to a very small change of x with time, quasi-steady-state conditions can be assumed (18) allowing thus the integration of Equation (14)

$$N = -D \left(\Delta C/x\right) \tag{15}$$

To obtain relative diffusion rates of solutes A and B through the same solvent, Equation (15) can be written for each solute, equated, and simplified in the following manner

$$\frac{N_A}{N_B} = \frac{D_A \quad \Delta C_A/x}{D_B \quad \Delta C_B/x} = \frac{D_A \; C_{sA}/M_A}{D_B \; C_{sB}/M_B} \tag{16}$$

Equation (16) indicates that if solubility and diffusion coefficients of solutes in a solvent are known, the relative diffusion rates of these solutes, and consequently the effective interface composition of their mixture diffusing from a capillary can be determined.

Finally, the question of the effective concentration gradient between the capillary entrance and the multi-component interface must be resolved. If only a single-component solute is present, the entire interface is equally active, and the effective concentration at that point is that of the saturated solution. In case of a multi-component mixture, each solute occupies but a fraction of the receding interface in the capillary limiting thus proportionally escaping tendency of the solute. In the dynamic system described, therefore, as first approximation, the interface concentration may be assumed equal to the sum of the products of solubility and fraction of each component at the interface

$$C_{sm} = C_{sA}n_A + C_{sB}n_B \tag{17}$$

Through introduction of a correction factor into Equation (17) to account for a possible change in solubility of solutes due to mixing, final expression describing effective concentration of a mixed solute at the interface is obtained

$$C'_{sm} \quad \left(C_{sA}n_A + C_{sB}n_B \right) \left(\frac{C_{sM}}{C_{sA} + C_{sB}} \right) \tag{18}$$

By virtue of experimental conditions employed, Equation (18) represents also effective concentration gradient to be used in the evaluation of the diffusivity of mixed solutes from the capillaries.

The introduced concepts of the effective interface composition and of the effective concentration form the basis for the evaluation of the diffusion coefficients of the multi-component solutes by means of the experimental method developed by Pirot and his co-workers (25). Once experimentally proven, they will supply the necessary verification of the mechanism by which a mixed solute diffuses from a solid interface into the solvent.

EXPERIMENTAL

1. Apparatus and Procedure

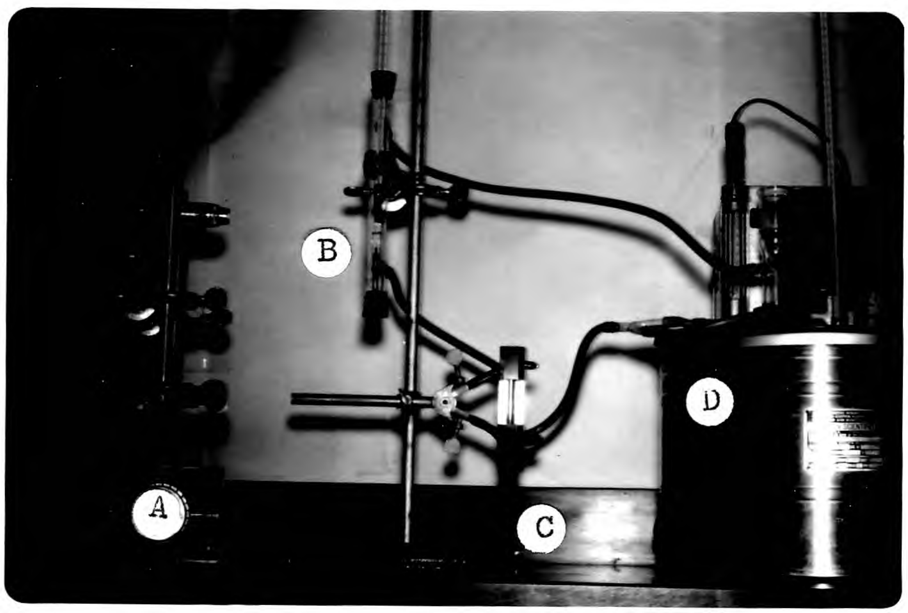
The experimental procedure employed melting point capillaries, about 0.1 cm in diameter, and 2.0 cm in length. At the beginning of each run, a capillary sealed at one end, was weighed accurately on an analytical balance, filled with distilled water under vacuum, and re-weighed to determine its exact volume. After a thorough drying, the capillary was loaded uniformely with a powdered solid. To accomplish this, a small increment of powder was introduced a little at a time and tamped with a close fitting steel mandrel. The capillary was placed in a small flask, submitted to a 2 mm Hg vacuum, or less, and covered with a saturated solution of the solid. Upon releasing the vacuum, solution was forced into the solid interstices formerly occupied by air. The density of loading and composition were then calculated from known volume of capillary, weight of loading, specific gravity of solid, and specific gravity of its saturated solution. This procedure in preference to that described by Piret and co-workers (25) was adopted because of considerable effect of supersaturation observed when saturated solution was subjected to vacuum.

The apparatus shown in Figure 3 and 4 consisted essentially of an extraction tube, a rotameter, a magnifying glass, and a solvent reservoir. The decision to use a relatively large but finite solvent volume

Figure 3

Apparatus for Extraction of Solid Solutes

from Capillaries



Key

A. Magnifying glass

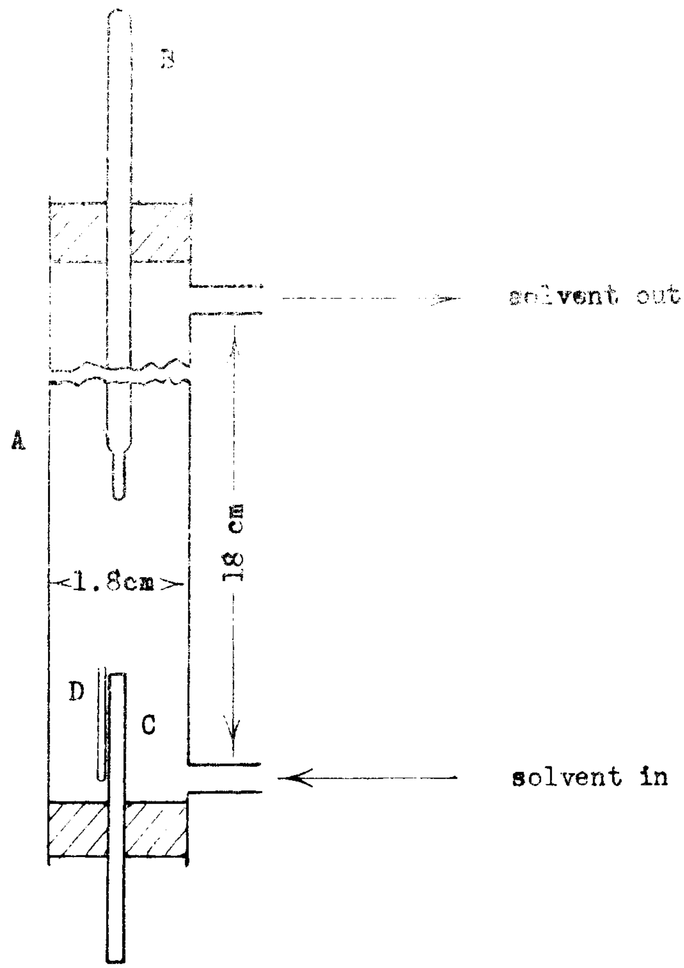
B. Extraction tube

C. Rotameter

D. Constant temperature bath

Figure 4

Extraction Tube



Key

A. Glass tube

B. Thermometer

C. Scale, calibrated in millimeters

D. Capillary, fastened to the scale

was made for practical reason to enable better temperature control, as well as, the application of solvents other than water.

The ten liter constant temperature bath, which served as a solvent reservoir, was equipped with an agitator, submerged circulation pump, and a thermostat, controlling temperature at 25 ± 0.011°C (± 0.02°F).

The magnifying glass used was a Flash-O-Lense mounted on an adjustable stand. A scale etched directly on the lens enabled readings accurate to 0.0025 cm.

In normal operation, a capillary loaded with a two-phase system was fastened to a scale calibrated in millimeters in such a manner as to protrude with the open end one millimeter above the scale, and inserted into the bottom of the extraction tube. The circulation of the solvent was then begun, and continued for several days, keeping the temperature constant at 25 ± 0.011°C. The level of solid in the capillary in relation to the capillary entrance was observed at intervals by means of the Flash-O-Lense and recorded. To test the results, a logarithmic plot of level drop of the solute bed versus time was prepared, as shown in Figure 5 for Runs # 11 and # 12.

2. Evaluation of Experimental Procedure

Before the final procedure was adopted, several effects which might cause experimental error were investigated. Factors considered were : direction of solvent circulation, rate of solvent circulation, turbulence at the capillary entrance, capillary diameter, density of capillary loading, and position of capillary in the extraction tube.

Intensity of turbulence at the capillary entrance was studied by circulating water through the extraction tube past capillaries filled with ink. Instantaneous penetration of solvent deep into the capillary was observed with practically all flow rates directed downward toward the capillary entrance. A similar effect occured with upward flows in excess of 760 cc./min., corresponding to the turbulent flow region. Circulation upward below this rate, on the other hand, produced very little turbulence, causing a maximum solvent penetration into the capillary of about 0.002 cm. only.

Quantitative performance of the apparatus was evaluated with the sodium chloride-water system. A series of experimental runs were made and the diffusivity of sodium chloride in water under diverse operating conditions was determined. The results are summarized in Table I.

The effects of capillary diameter and of capillary loading were studied in Runs #6 and #7. Within limits tested neither was found to have any influence on the experimental diffusivity value.

Table I

Evaluation of the Experimental Method

Solute : Sodium chloride

Solvent : Water

Temperature : $25 \pm 0.011^{\circ}C$

Run #	Water Circulation Direction	Rate (cc./min.)	Capillary Inside Dia. (mm.)	Loading a	D_e x10^5 (sq.cm./sec.)
1a	downward	40	1.37	0.591	1.40
1b	"	40	1.37	0.602	1.42
1c	"	40	1.33	0.631	1.38
2	"	130	1.40	0.664	1.55
3	"	300	1.40	0.547	1.62
4	"	2000	1.37	0.612	2.22
5	upward	40	1.40	0.629	1.33
6a	"	120	0.85	0.611	1.52
6b	"	120	0.98	0.624	1.54
6c	"	120	1.38	0.622	1.52
7a	"	150	1.40	0.646	1.54
7b	"	150	1.40	0.636	1.52
7c	"	150	1.40	0.596	1.53
8	"	300	1.40	0.650	1.54
9	"	600	1.40	0.613	1.53
10	"	2000	1.40	0.620	1.88

Runs #1 through #4 demonstrated extreme sensitivity of the apparatus to downward flow. They indicated that under such conditions the true diffusion coefficient can hardly be obtained due to its strong dependence on the flow rate.

Slow circulation of water employed during Runs # 1 and # 5 produced low diffusion coefficients, probably due to the formation of a stagnant layer immediately outside the capillary entrance.

With turbulent flow rates of Runs # 4 and # 10, abnormally high diffusion coefficients were determined indicating solvent penetration into the capillary.

Consistent diffusivity of proper magnitude obtained with all experimental runs using upward circulation between 120 cc./min. and 600 cc./min. indicated formation of the desired flow pattern at the capillary entrance. On this basis upward flow rate of 300 cc./min. was selected for further experimental work.

The data of Table I suggest that an excellent duplication of results with the given set-up was possible. This is shown by diffusion coefficient values calculated from Runs # 6 through # 9, under the conditions of which variation of the experimental diffusion coefficient of sodium chloride did not exceed 1.53 $\times 10^{-5}$ sq.cm./sec. $\pm$ 0.65 %.

Further checks with sucrose, potassium sulfate, and cupric sulfate pentahydrate verified satisfactory performance of the apparatus. The diffusion coefficients of these materials calculated from experimental data of Figure 5 compare well with values determined by other investigators (19,25,29,30,31).

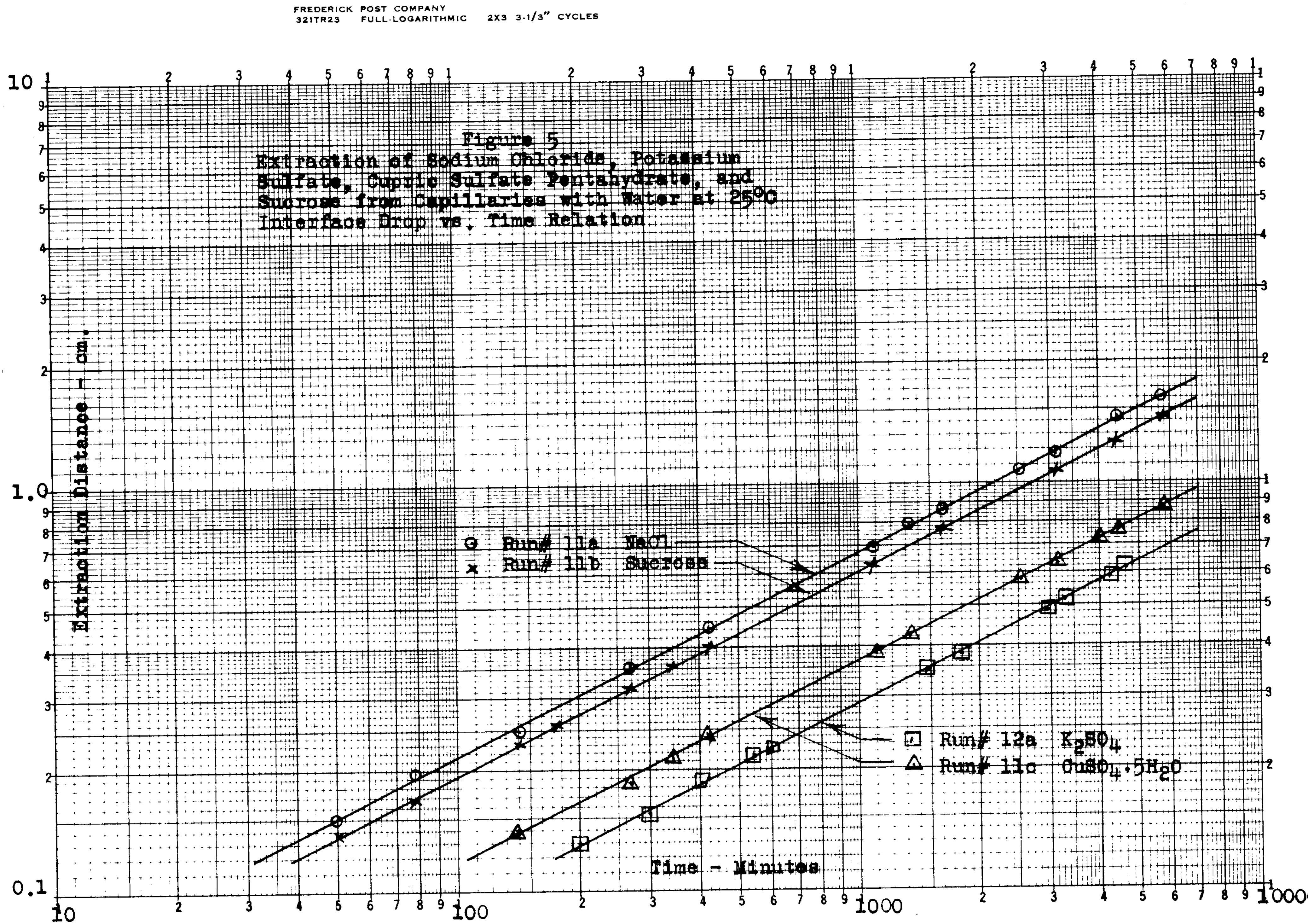

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Figure 5
Extraction of Sodium Chloride, Potassium Sulfate, Cupric Sulfate Pentahydrate, and Sucrose from Capillaries with Water at 25°C
Interface Drop vs. Time Relation
Extraction Distance - cm.
Time - Minutes
Run# 11a NaCl
Run# 11b Sucrose
Run# 12a K2SO4
Run# 11c CuSO4·5H2O
10
1.0
0.1
10
100
1000
10000

Table II

Evaluation of the Experimental Method

Solvent : Water
Temperature : 25 ± 0.011°C
Circulation Rate : 300 cc/min., Upward

Run #	Solute	Capillary Loading ρ_a (gm/cc)	Capillary Loading a (cc/cc)	Experimental D_e $\times 10^5$ (sq.cm/sec.)	From Literature D_r $\times 10^5$ (sq.cm/sec.)	From Literature Reference
11a	Sodium cloride	1.397	0.645	1.534	1.55	25
					1.52-1.61	29
					1.526	30
11b	Sucrose	1.053	0.665	0.244	0.263-0.288	25
					0.24	19
11c	Cupric sulfate pentahydrate	1.557	0.683	0.492	0.499-0.504	25
12a	Potassium sulfate	2.185	0.823	1.25	1.24 -1.34	31

DISCUSSION OF RESULTS

1. Single - Component Solutes

The experimental work was done with three components of cranberry skins, soluble in methyl isobutyl ketone: ursolic acid, palmitic acid, and tripalmitin. The purpose of the extraction of these compounds from capillaries was to determine their diffusion coefficients in methyl isobutyl ketone, to compare these values with data from literature, and to establish in such a manner a sound basis for further experimental work with mixed solutes.

Employing the previously described method, two-phase mixtures of palmitic acid, ursolic acid, and tripalmitin were extracted from capillaries during Runs # 21a, 21b, and 21c, respectively. In the course of extraction sharp gradually receding solid-liquid boundaries were ontained enabling an accurate reading of the rate of interface drop with time. Plotted in Figure 6 these data gave straight lines of 0.5 slope required by Equation (13) to verify that diffusion took place and was rate controlling.

Diffusion coefficients of palmitic acid, ursolic acid, and tripalmitin were calculated from experimental data, and compared with values determined by means of the empirical Wilke correlation (31). Sample Calculations # 1 and # 2 describe the methods. Results summarized in Table III indicate a satisfactory agreement between the experimental and the estimated values. Slightly lower diffusion coefficients of palmitic acid and tripalmitin obtained experimentally suggest the effect of solute on the viscosity of solvent which was neglected by the Wilke correlation. On the other hand, higher experimental diffusivity of ursolic acid can be explained by the abnormal behavior of its solid-saturated solution mixture, which in the presence of a limited amount of methyl isobutyl ketone had a tendency to transform into a hard, semi - transparent, quasi - homogenous substance. Apparently, the solubility of ursolic acid in methyl isobutyl ketone under such conditions is somehow effected.

The performance of the apparatus with methyl isobutyl ketone was found to be as satisfactory as with water. The experimental diffusion coefficients of different solutes obtained in these two solvents indicated also that the method is appliable, equally well, to polar and non-polar systems.

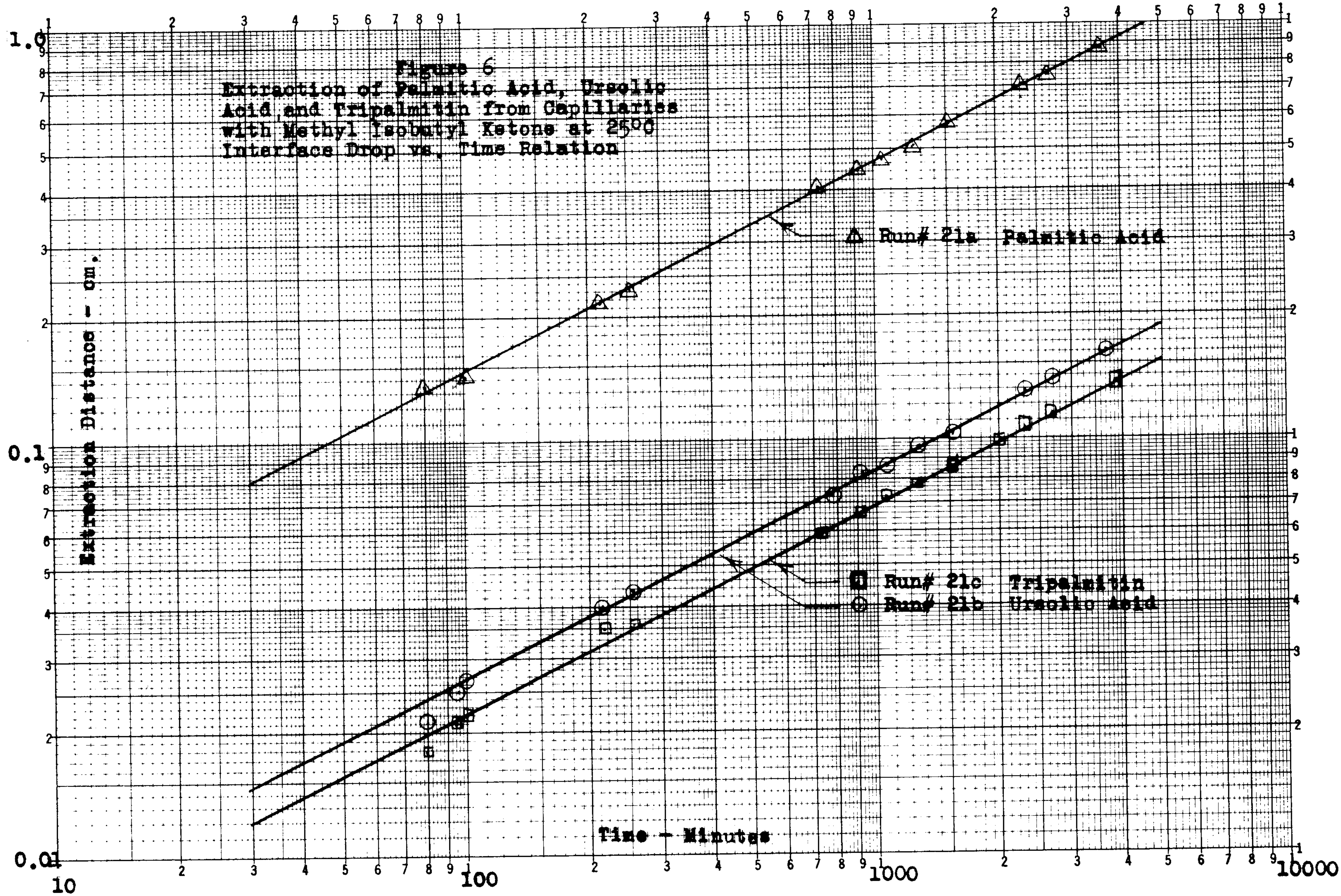

Figure 6
Extraction of Palmitic Acid, Ursolic Acid and Tripalmitin from Capillaries with Methyl Isobutyl Ketone at 25°C
Interface Drop vs. Time Relation

Table III

Diffusion Coefficients of Single-Component

Solutes in Methyl Isobutyl Ketone

at 25°C

Run#	Solute	ρ_a $\left(\frac{gm.}{cc.}\right)$	a	C_s $\left(\frac{gm.}{cc.}\right)$	D_e x10^5 $\left(\frac{sq.cm.}{sec.}\right)$	D_w x10^5 $\left(\frac{sq.cm.}{sec.}\right)$	$\left(\frac{D_e - D_w}{D_e}\right)$ x100 %Deviation
21a	Palmitic acid	0.723	0.782	0.1124	1.110	1.162	-4.7
21b	Ursolic acid	0.717	0.741	0.00413	1.037	0.903	+12.9
21c	Tripalmitin	0.629	0.683	0.00448	0.567	0.583	-2.8

2. Multi-Component Solutes

The primary objective of current investigation was to find a relation between the diffusivity and the composition of solutes diffusing from a solid-liquid interface. To study such systems, samples of palmitic acid, ursolic acid, and tripalmitin were blended in various proportions, placed into the capillaries, then extracted with methyl isobutyl ketone in a manner similar to that applied to single-component solutes. In each case the initial capillary charge consisted of a two-phase mixture of a solute of known composition, and of its saturated methyl isobutyl ketone solution. It should be noted that the term "multi-component solute" or "mixed solute" was used in this paper to describe the mixture of two or more single-component solutes only. The solvent, although present in the solid-liquid mixture initially charged into the capillary, was not considered as one of the solutes because it did not diffuse in the same direction with other solutes during the extraction.

Figures 7, 8, and 9 present experimental data from Runs # 22, and # 23 during which several two-component, and one three-component mixture of palmitic acid, ursolic acid, and tripalmitin were extracted. Formation of sharp, gradually receding boundaries was observed, indicating that extraction of each component in the mixture has taken place from the solid-liquid interface at the rate proportional to the composition of the solute bed, as postulated. On this basis diffusion coefficients of mixed solutes were computed from experimental data

Runs # 1 through # 4 demonstrated extreme sensitivity of the apparatus to downward flow. They indicated that under such conditions the true diffusion coefficient can hardly be obtained due to its strong dependence on the flow rate.

Slow circulation of water employed during Runs # 1 and # 5 produced low diffusion coefficients, probably due to the formation of a stagnant layer immediately outside the capillary entrance.

With turbulent flow rates of Runs # 4 and # 10, abnormally high diffusion coefficients were determined indicating solvent penetration into the capillary.

Consistent diffusivity of proper magnitude obtained with all experimental runs using upward circulation between 120 cc./min. and 600 cc./min. indicated formation of the desired flow pattern at the capillary entrance. On this basis upward flow rate of 300 cc./min. was selected for further experimental work.

The data of Table I suggest that an excellent duplication of results with the given set-up was possible. This is shown by diffusion coefficient values calculated from Runs # 6 through # 9, under the conditions of which variation of the experimental diffusion coefficient of sodium chloride did not exceed 1.53×10^{-5} sq.cm./sec. ± 0.65 %.

Further checks with sucrose, potassium sulfate, and cupric sulfate pentahydrate verified satisfactory performance of the apparatus. The

The verification of the experimental results by the data from literature enhances their validity. It not only proves the relation between the diffusivity and the composition of solutes, but also justifies, indirectly, the use of the proposed concept of the interface composition for the calculation of the diffusion coefficients of mixed solutes from experimental data, as well as, substantiates the mechanism of diffusion of mixed solutes from a solid-liquid interface. In such a manner a better insight into the nature of this phenomenon is secured.

The established relationship between the diffusivity and the composition enables prediction of the diffusion coefficients of solutes. The method should prove especially valuable to multi - component solutes where experimental data are practially non - existent.

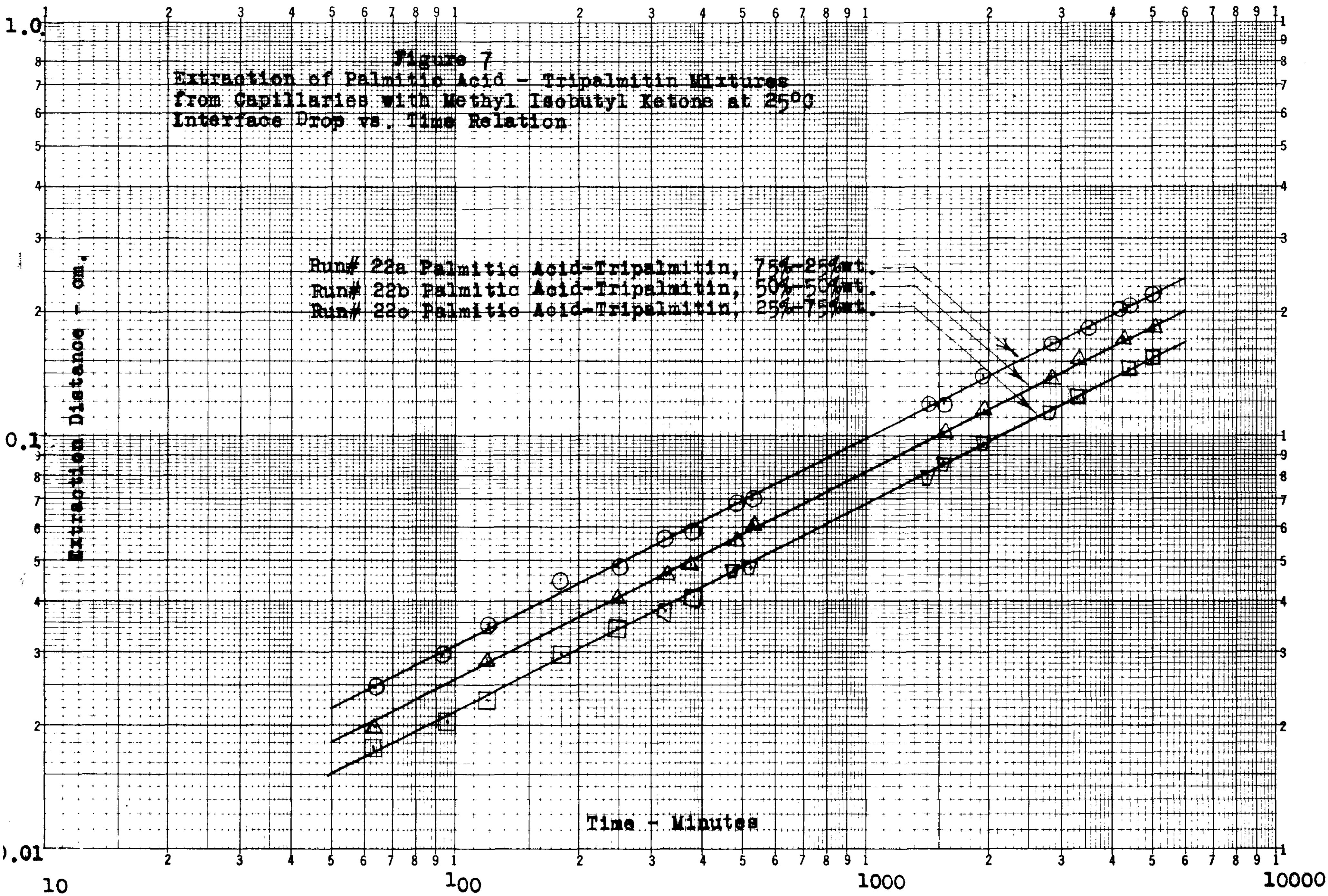
Figure 7
Extraction of Palmitic Acid - Tripalmitin Mixtures from Capillaries with Methyl Isobutyl Ketone at 25°C
Interface Drop vs. Time Relation
Run# 22a Palmitic Acid-Tripalmitin, 75%-25%wt.
Run# 22b Palmitic Acid-Tripalmitin, 50%-50%wt.
Run# 22c Palmitic Acid-Tripalmitin, 25%-75%wt.
Extraction Distance - cm.
Time - Minutes
1.0
0.1
0.01
10
100
1000
10000

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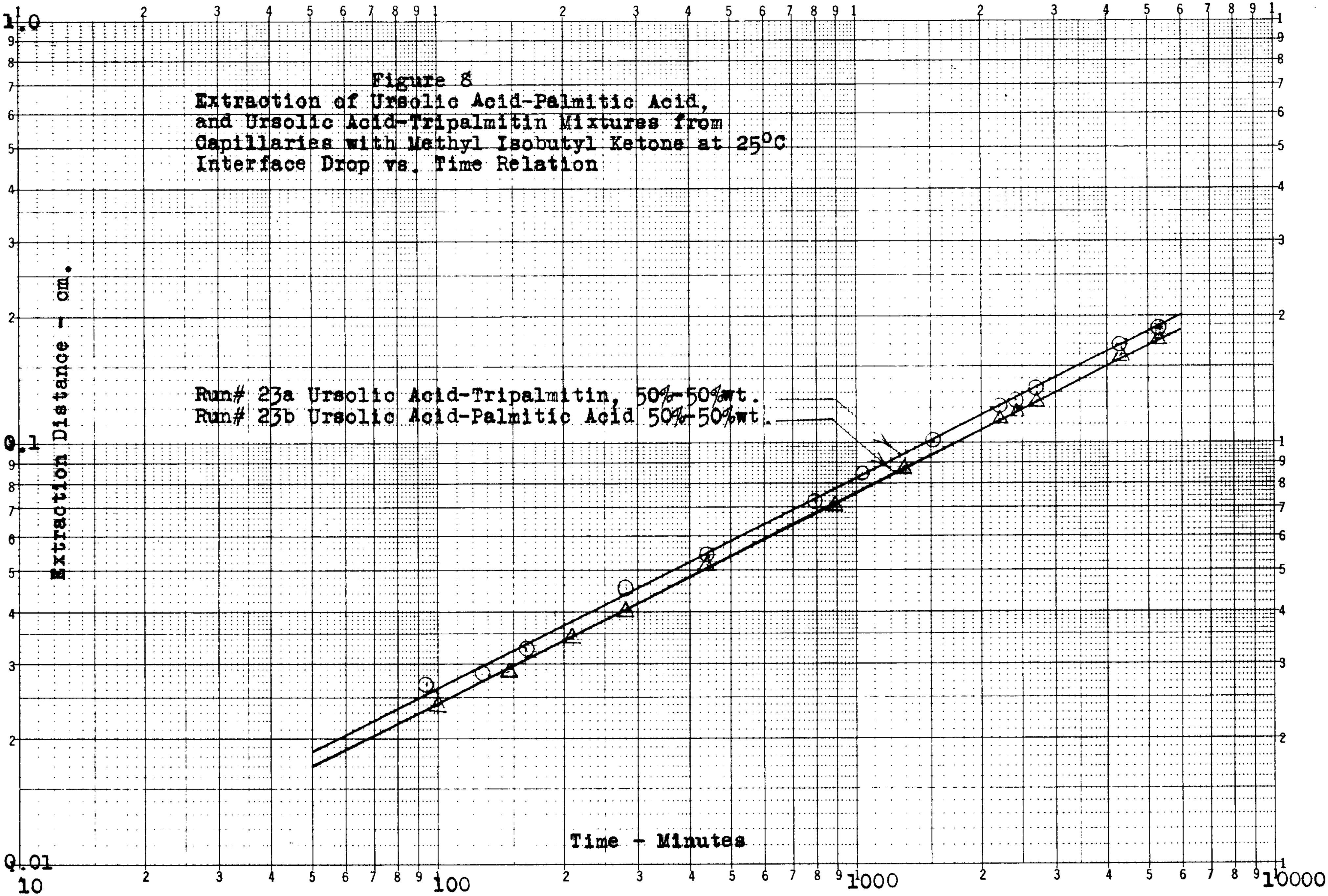

Figure 8
Extraction of Ursolic Acid-Palmitic Acid, and Ursolic Acid-Tripalmitin Mixtures from Capillaries with Methyl Isobutyl Ketone at 25°C
Interface Drop vs. Time Relation

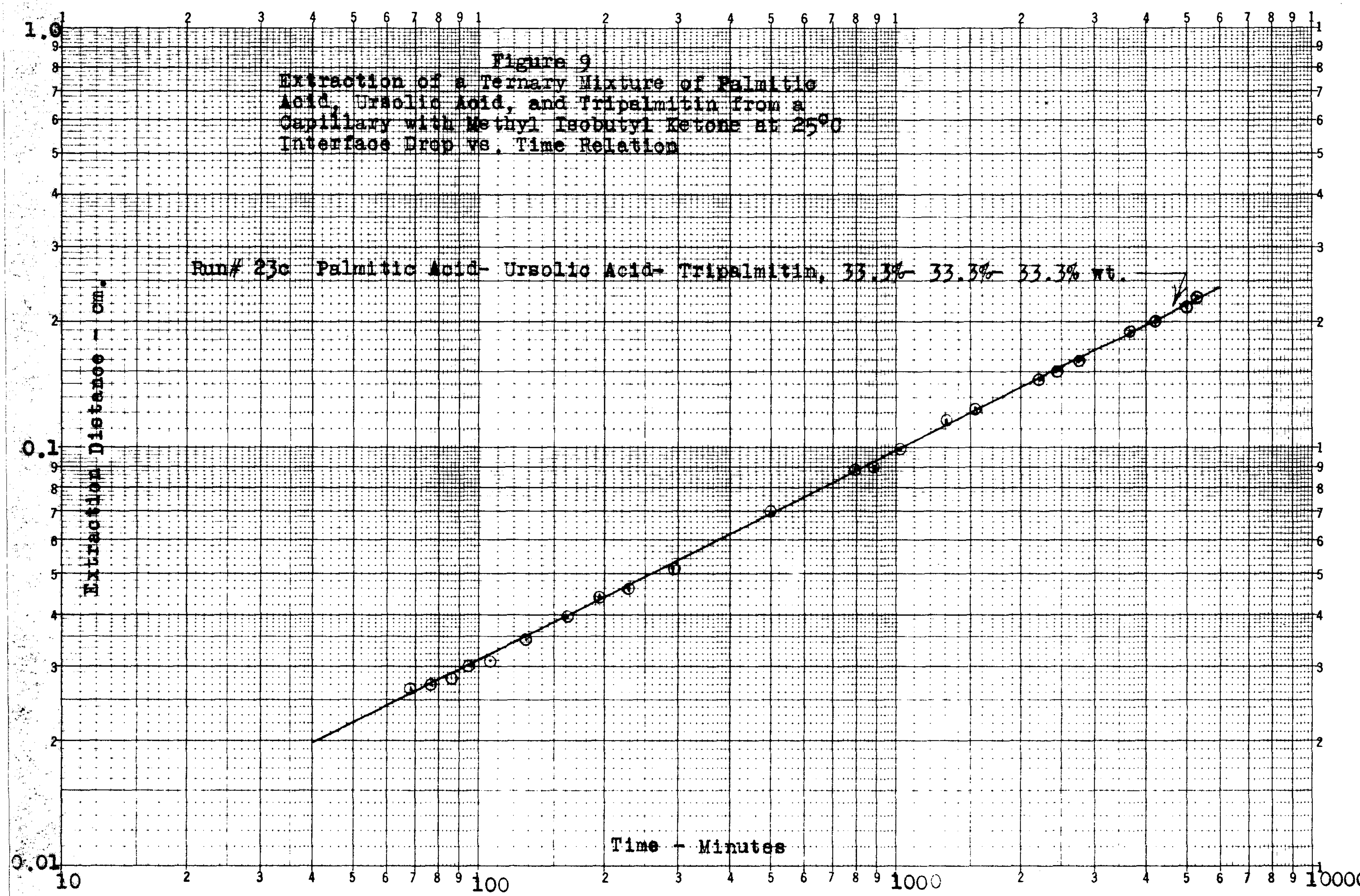
Figure 9
Extraction of a Ternary Mixture of Palmitic Acid, Ursolic Acid, and Tripalmitin from a Capillary with Methyl Isobutyl Ketone at 25°C
Interface Drop vs. Time Relation
Run# 23c Palmitic Acid- Ursolic Acid- Tripalmitin, 33.3%- 33.3%- 33.3% wt.
Extraction Distance - cm.
Time - Minutes
1.0
0.1
0.01
10
100
1000
10000

Table IV

Diffusion Coefficients of Multi-Component Solutes in Methyl Isobutyl Ketone at 25°C

Run #	Solute	Composition of Solid Solute: In Solute Bed (weight %)	(mole %)	At Interface (x) (weight %)
21a	Palmitic acid -Tripalmitin	100-0	100-0	100-0
22a	"	75-25	90.4-9.6	1.9-98.1
22b	"	50-50	75.9-24.1	0.64-99.36
22c	"	25-75	51.2-48.8	0.22-99.78
21c	"	0-100	0-100	0-100
23a	Ursolic acid -Tripalmitin	50-50	63.8-36.2	25.2-74.8
23b	Ursolic acid -Palmitic acid	50-50	35.9-64.1	98.11-1.89
23c	Palmitic acid -Ursolic acid -Tripalmitin	33.3 -33.3 -33.3	53,2 -29.9 -16.9	0.48 -25.12 -74.40

(x) Interface between the solute bed and the solvent; composition of interface estimated on the basis of relative diffusion rates of solutes in mixture.

Table IV (Continued)

Diffusion Coefficients of Multi-Component Solutes in Methyl Isobutyl Ketone at 25°C

Run #	C'_{sm} $\left(\frac{gm}{cc}\right)$	ρ_a $\left(\frac{gm}{cc}\right)$	a	$D_e x10^5$ $\left(\frac{sq\ cm}{sec}\right)$	$D_s x10^{-5}$ $\left(\frac{sq\ cm}{sec}\right)$	$\left(\frac{D_e - D_s}{D_s}\right)$ x100 (%Deviation)[xx]
21a	0.1124	0.723	0.782	1.110		
22a	0.00600	0.783	0.847	1.048	1.040	+ 0.8
22b	0.00474	0.820	0.839	0.950	0.940	+ 1.1
22c	0.00431	0.876	0.950	0.782	0.803	-2.6
21c	0.00448	0.629	0.683	0.567		
23a	0.00507	0.748	0.789	0.828	0.838	-1.2
23b	0.00343	0.781	0.826	1.093	1.080	+ 1.2
23c	0.00381	0.466	0.497	0.978	0.970	+ 0.8

(xx) Deviation from straight line relation between the diffusion coefficient and the solute composition (Refer to Figures 10,11, and 12).

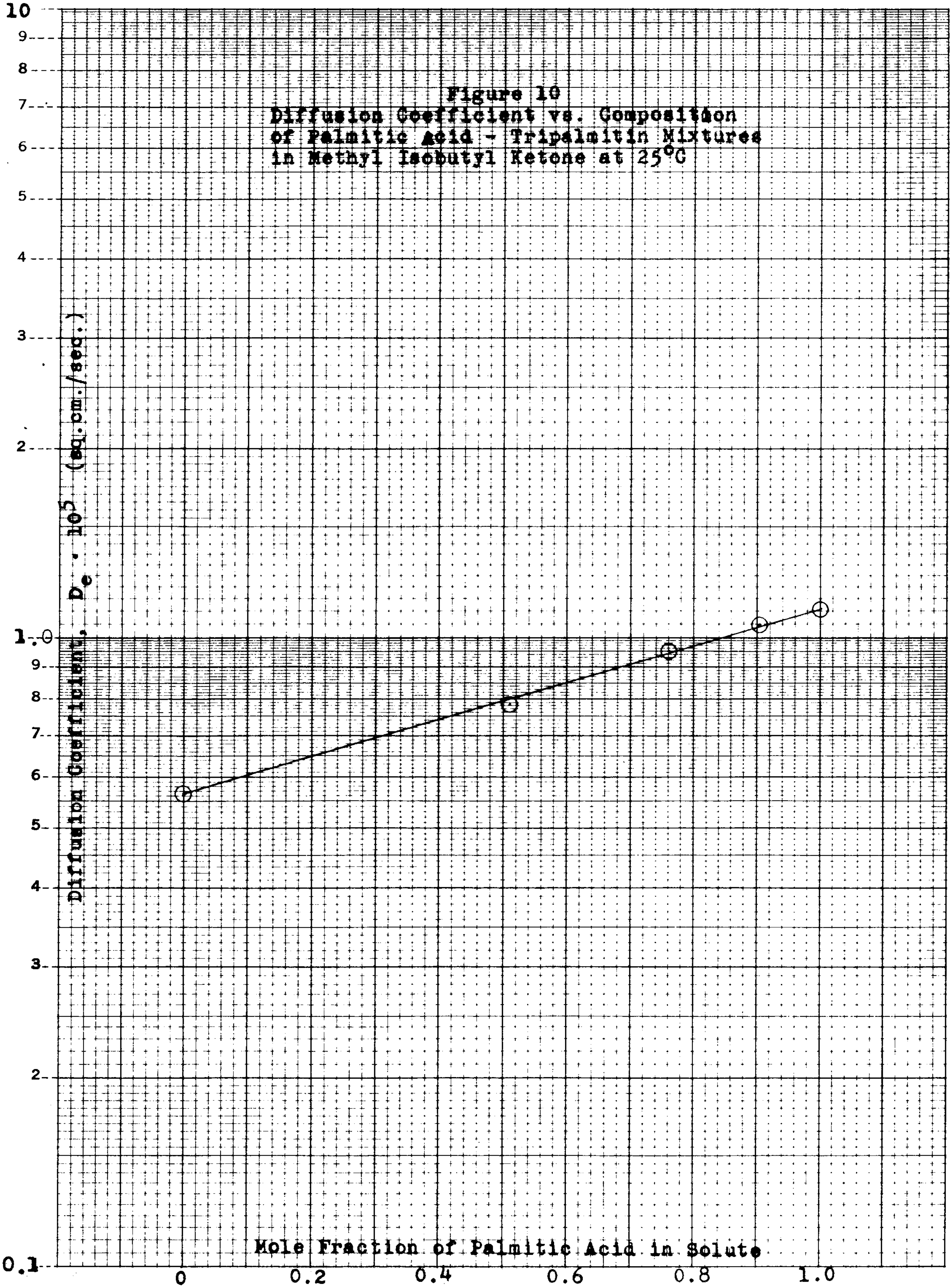
Figure 10
Diffusion Coefficient vs. Composition
of Palmitic Acid - Tripalmitin Mixtures
in Methyl Isobutyl Ketone at 25°C
Diffusion Coefficient, $D_e \cdot 10^5$ (sq.cm./sec.)
Mole Fraction of Palmitic Acid in Solute
10
9
8
7
6
5
4
3
2
1.0
9
8
7
6
5
4
3
2
0.1
0
0.2
0.4
0.6
0.8
1.0

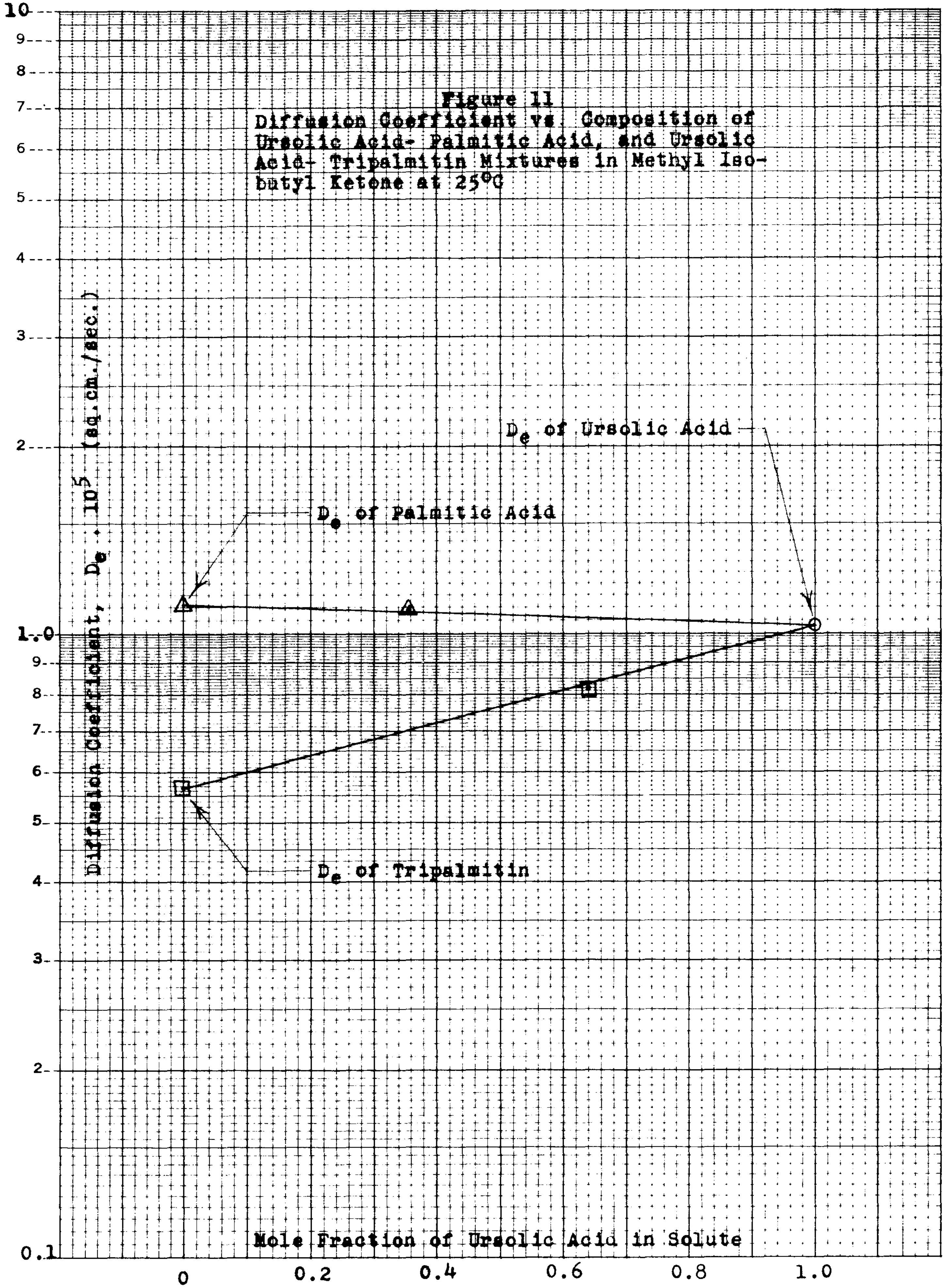

Figure 11
Diffusion Coefficient vs. Composition of Ursolic Acid- Palmitic Acid, and Ursolic Acid- Tripalmitin Mixtures in Methyl Isobutyl Ketone at 25°C

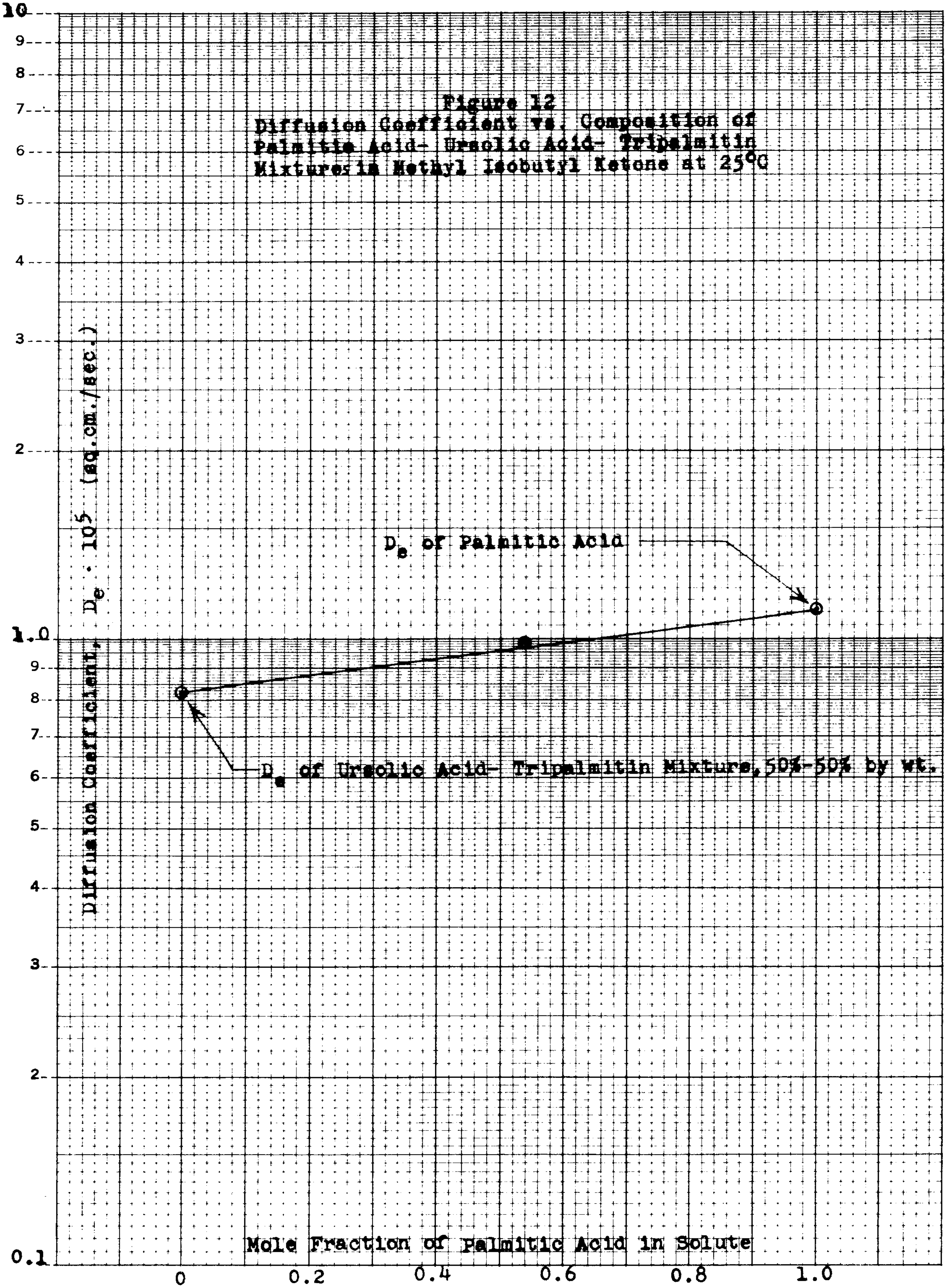

Figure 12
Diffusion Coefficient vs. Composition of Palmitic Acid- Ursolic Acid- Tripalmitin Mixtures in Methyl Isobutyl Ketone at 25°C

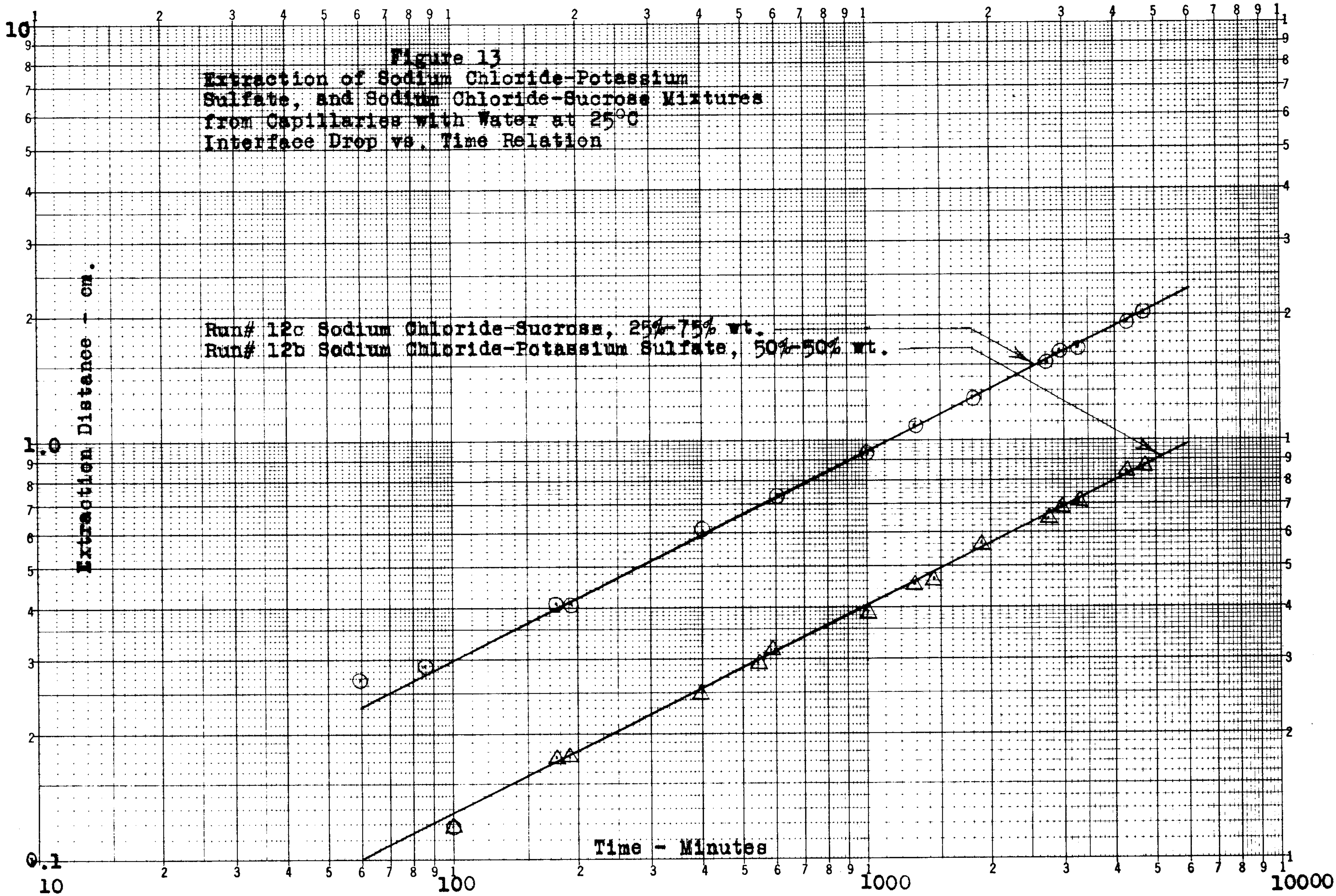
Figure 13
Extraction of Sodium Chloride-Potassium
Sulfate, and Sodium Chloride-Sucrose Mixtures
from Capillaries with Water at 25°C
Interface Drop vs. Time Relation
Run# 12c Sodium Chloride-Sucrose, 25%-75% wt.
Run# 12b Sodium Chloride-Potassium Sulfate, 50%-50% wt.
Extraction Distance - cm.
Time - Minutes
10
1.0
0.1
10
100
1000
10000

Table V

Diffusion Coefficients of Multi-Component Solutes in Water at 25°C

Run#	Solute	Composition of Solid Solute In Solute Bed (Weight %)	(Mole %)	At Interface (x) (Weight %)
12b	Sodium chloride -Potassium Sulfate	50-50	74.9-25.1	9.24-90.76
12c	Sodium chloride - Sucrose	25-75	66.1-33.9	1.90-98.10

(x) Interface between the solute bed and the solvent;composition of interface estimated on the basis of relative diffusion rates of solutes in mixture.

Table V (Continued)

Diffusion Coefficients of Multi-Component Solutes in Water at 25°C

Run#	C'_{sm} $\left(\frac{gm}{cc}\right)$	ρ_a $\left(\frac{gm}{cc}\right)$	a	D_e x10^5 $\left(\frac{sq.cm}{sec}\right)$	D_s x10^5 $\left(\frac{sq.cm}{sec}\right)$	$\left(\frac{D_e-D_s}{D_s}\right)$ x100 %Deviation (xx)
12b	0.1243	1.420	0.589	1.46	1.44	+1.4
12c	0.827	1.023	0.591	0.604	0.828	-27.2

(xx) Deviation from straight line relation between the diffusion coefficient and the solute composition (Refer to Figure 14).

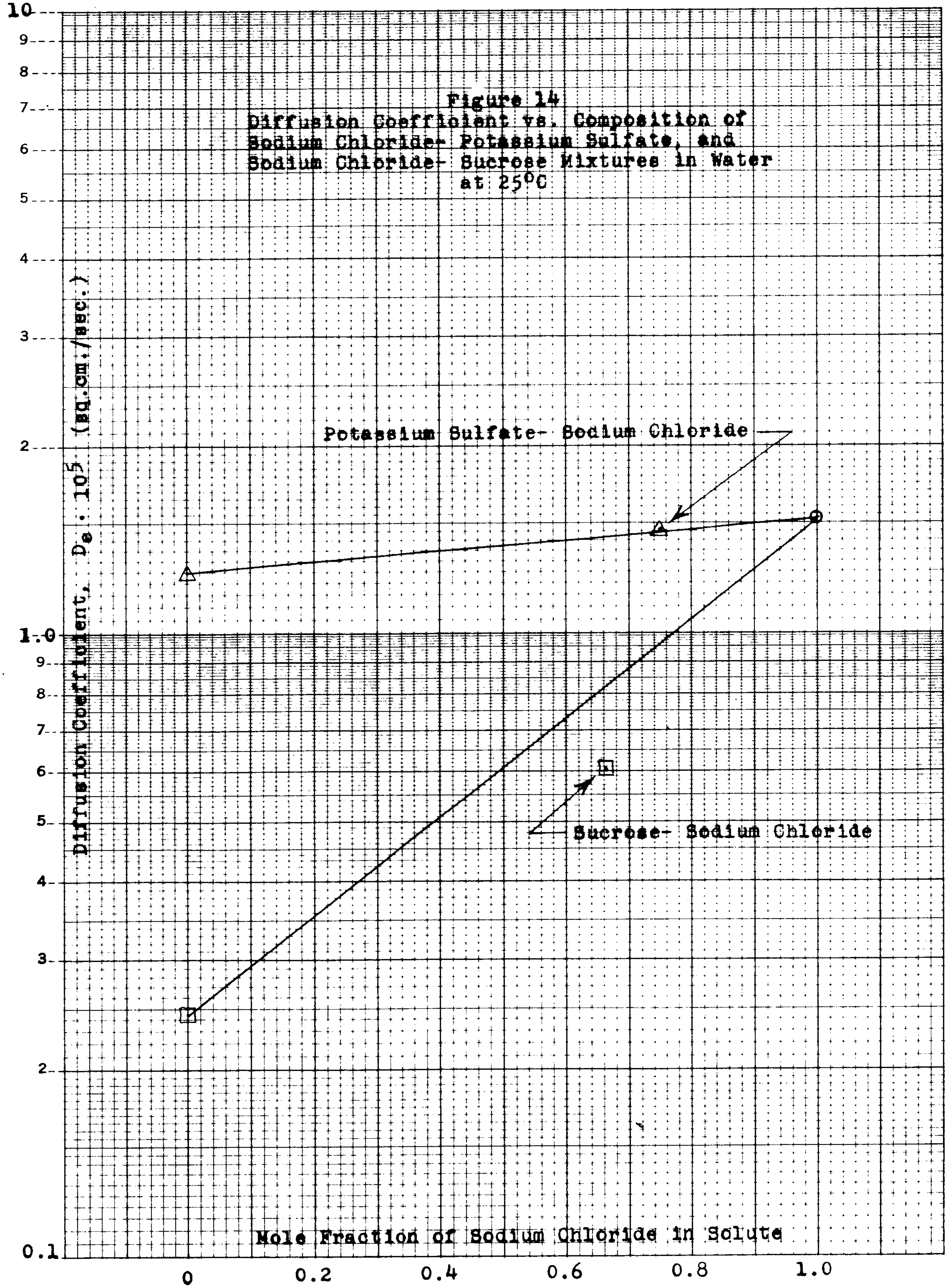

Figure 14
Diffusion Coefficient vs. Composition of Sodium Chloride- Potassium Sulfate, and Sodium Chloride- Sucrose Mixtures in Water at 25°C

Table VI

Diffusion Coefficients of Ions and Ionic Compounds in Water at 25°C (Ref.29)

Solute	Composition of Solute (mole %)	D_r x10^5 $\left(\frac{sq.cm.}{sec.}\right)$	D_s x10^5 $\left(\frac{sq.cm.}{sec.}\right)$	$\left(\frac{D_r-D_s}{D_s}\right)$ x100 (%Deviation)^x
H^+	100	9.32		
Na^+	100	1.332		
Ba^{++}	100	0.856		
Cl^-	100	2.025		
Hydrogen chloride	50-50	2.94	4.30	-31.6
Sodium chloride	50-50	1.61	1.65	-2.4
Barium chloride	33.3-66.7	1.44	1.51	-4.6

(x) Deviation from straight line relation between the diffusion coefficient and the solute composition (Refer to Figure 15)

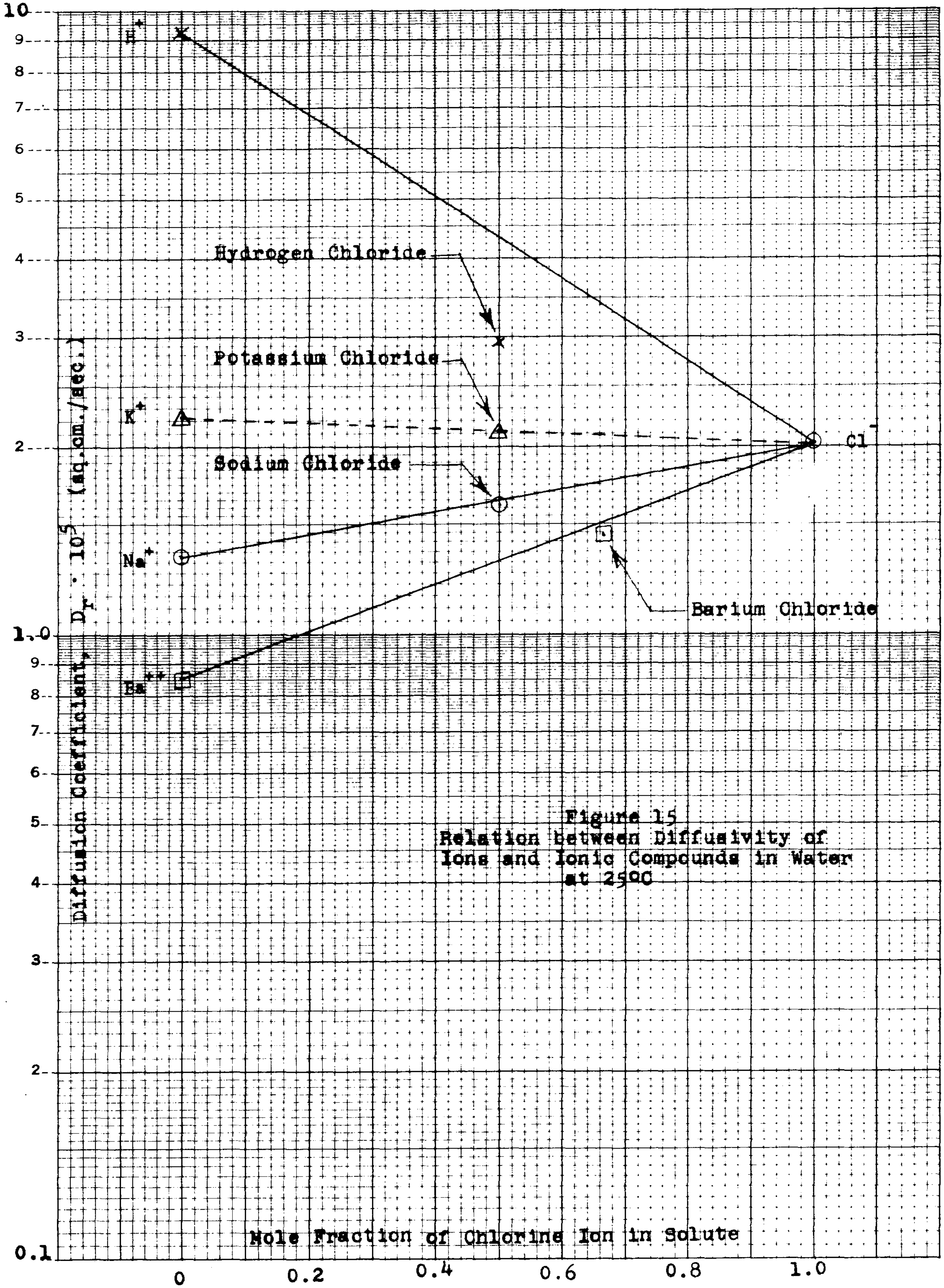

Figure 15
Relation between Diffusivity of Ions and Ionic Compounds in Water at 25°C

3. Diffusion Coefficient vs. Extraction Rate

The proper use of the diffusion coefficients to practical problems requires knowledge of their relation to the diffusion rate. An attempt was made to find such a relation. For this purpose the rate equation, represented by Fick's First Law, was employed. The applicability of the latter to the diffusion of solutes from a receding interface has been mentioned on Page 13, and discussed by other investigators (18).

The procedure described in Sample Calculation # 4, involved calculation of diffusion rates, N_e , directly from known composition of the solute bed and the rate of its level drop during the extraction. The values thus obtained were substituted into the Fick's First Law equation

$$N_e = D_f \left(\frac{\Delta C}{x_{av}} \right) \qquad (15)$$

and the apparent diffusion coefficients, D_f , determined. These coefficients were compared with the experimental diffusion coefficients in Table VII. The discrepancy between the two values indicated that for conditions encountered during leaching operation a certain deviation from Fick's Law exists. Plotted in Figure 16, this deviation was found to be a function of solubility. On this basis a generalized factor, Φ_L correcting for the deviation from Fick's Law, was established

$$\Phi_L = (1 + C_s^{1.6}) \qquad (19)$$

Literature search revealed that a similar factor correcting for the deviation from Fick's Second Law has been proposed by Arnold (1,3) for diffusion in an evaporating system. Both factors are compared in Table VIII.

Applying the proposed correction to the Fick's First Law equation, a simple relation between the experimental diffusion coefficient, D_e, and the actual diffusion rate, N_e, of a solute diffusing from a solid-liquid interface, was obtained

$$N_e = \left(\frac{\Delta C}{x_{av}}\right) D_f$$

$$= \left(\frac{\Delta C}{x_{av}}\right) D_e \, \phi_L$$

$$= \left(\frac{\Delta C}{x_{av}}\right) D_e \quad (1 + C_s^{1.6}) \tag{20}$$

The necessity for the correction factor lies in the fact that D_e represents diffusivity at infinite dilution, whereas, during the extraction studied diffusion has taken place between the saturated solution at the interface and the solution of negligible concentration at the capillary entrance.

It is to be noted that the established deviation from Fick's Law was found to hold equally well to single-, as well as, multi-component solutes. In the latter case, as could be expected from previous discussion, to calculate overall average extraction rates of mixed solutes, the use of the effective interface concentration, C'_{sm}, was necessary.

Table VII

Comparison of Experimental Diffusion Coefficients with Apparent Diffusion Coefficients Estimated from Extraction Rate Data Using Fick's First Law Equation

Run #	Solute	C_s $\left(\frac{gm}{cc}\right)$	D_e x10^5 $\left(\frac{sq.cm.}{sec.}\right)$	D_f x10^5 $\left(\frac{sq.cm.}{sec.}\right)$	$\left(\frac{D_f-D_e}{D_e}\right)$x100 %Deviation
12a	Potassium sulfate	0.1190	1.25	1.29	3.2
11b	Cupric sulfate .5H_2O	0.3128	0.492	0.565	15.2
11a	Sodium chloride	0.3171	1.534	1.796	17.6
11c	Sucrose	0.9050	0.244	0.458	87.7
21a	Palmitic acid	0.1124	1.110	1.148	3.4
21b	Ursolic acid	0.00413	1.037	1.047	1.0
21c	Tripalmitin	0.00448	0.567	0.580	2.3
12b	Sodium chloride -Potassium sulfate, 50-50% wt.	0.398	1.36	1.60	24.[illegible]
12c	Sodium chloride -Sucrose, 25-75% wt.	1.136	0.368	0.753	119.0
22b	Palmitic acid -Tripalmitin, 50-50% wt.	0.1070	0.782	0.800	2.6%

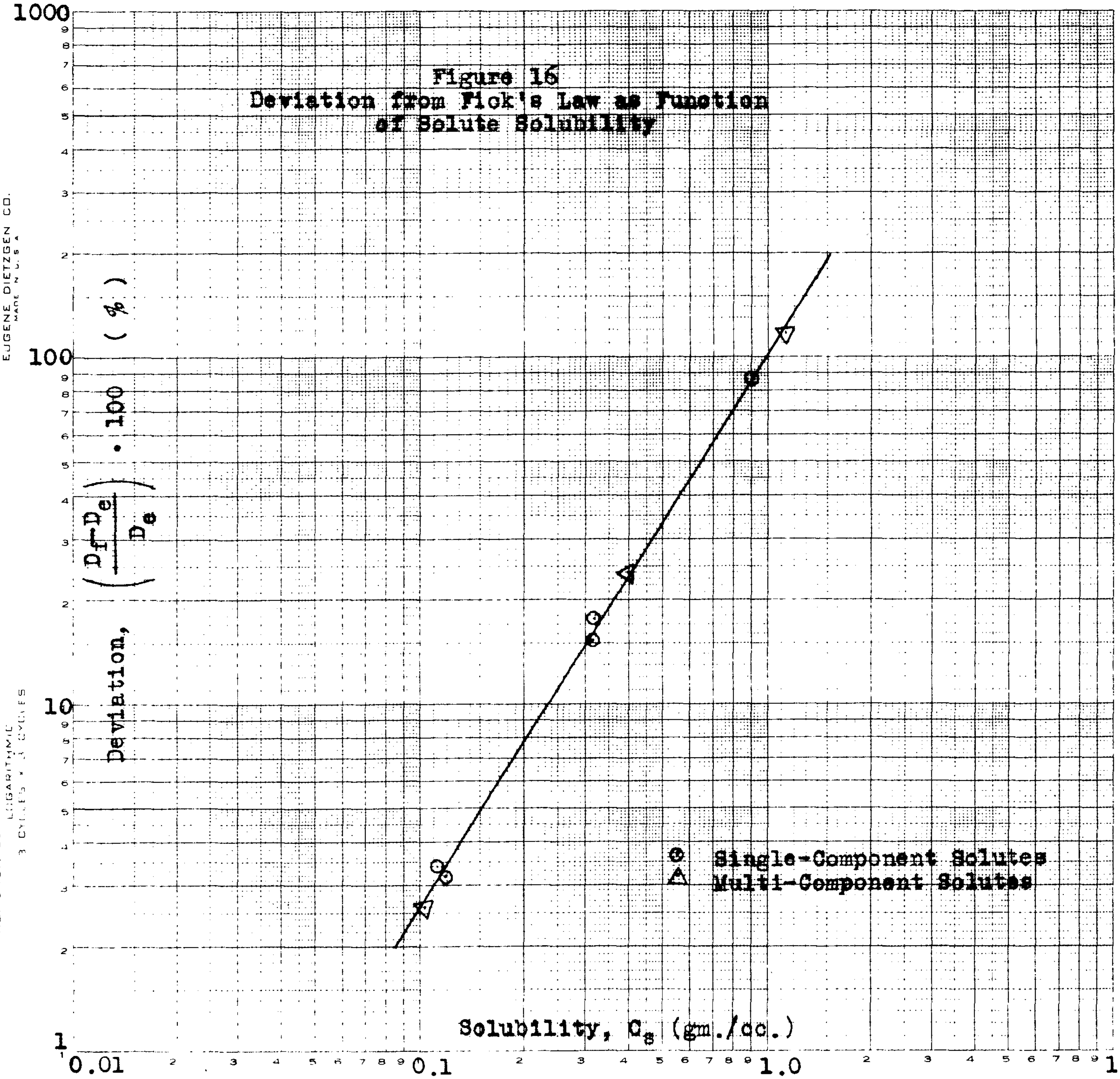
Figure 16
Deviation from Fick's Law as Function
of Solute Solubility
Deviation, $\left(\frac{D_f - D_e}{D_e}\right) \cdot 100$ (%)
Solubility, C_s (gm./cc.)
Single-Component Solutes
Multi-Component Solutes
1000
100
10
1
0.01
0.1
1.0
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Table VIII

Comparison of Factors Indicating Deviation from Fick's Law for Diffusion in Liquids and Vapors.

Solid-Liquid System		Liquid - Vapor System(1,3)	
C_s (gm/cc)	Factor, Φ_L $(1 + C_s^{1.6})$	y_o (mole fraction)	Factor, Φ_V $1/(1-y_o)^{2/3}$ approx.
0.0	1.00	0.0	1.00
0.25	1.109	0.25	1.108
0.50	1.330	0.50	1.298
0.75	1.596	0.75	1.564
1.00	2.000	1.00	∞

CONCLUSION

The value of current investigations lies in the comprehensive study of the liquid phase extraction from capillaries, during which diffusion coefficients of several single - and multi-component solutes were determined, and the relations between the diffusivity, the solute composition, and the extraction rate established.

The experimental method of Piret, Ebel, Kiang and Armstrong (25), adopted for the evaluation of the diffusion coefficients of solutes, was throughly tested with known sodium chloride - water system. The procedure, involving extraction of two-phase mixtures from capillaries, was found to be especially suitable for the study of leaching operations. The duplication of the results within ±0.65% proved the reliability of the method, and of the apparatus used. The diffusion coefficients of several salts and of sucrose in water determined experimentally were of the same order of magnitude as those found in literature.

Extended to non - aqueous media the method was shown to be generally applicable to ionic, as well as, non-ionic systems. The diffusion coefficients of ursolic acid, palmitic acid, and tripalmitin determined in methyl isobutyl ketone compared favorable with values estimated by the empirical Wilke correlation (31).

The extraction of multi-component solutes from capillaries indicated a diffusional operation governed by the composition of the solute at the solid-liquid interface. On this basis, the diffusion coefficients of mixed solutes were calculated from experimental data using the introduced concept of the effective interface composition. A straight line relation between the diffusivity and the solute composition was obtained and verified with most systems tested. The order of magnitude of the diffusion coefficients, and the data from literature further verified this relation. The established relation is expected to enable a fairly accurate prediction of the diffusion coefficients of solutes. For instance, from known diffusion coefficients of potassium chloride and chlorine ion, the diffusivity of potassium ion in water at 25°C can be estimated at 2.22 $\times 10^{-5}$ sq.cm./sec., as shown in Figure 15. The method should prove especially valuable in the estimation of the diffusion coefficients of mixed solutes where experimental data are practially non-existent.

The relation between the experimental diffusivity and the extraction rate was determined by means of the Fick's First Law equation. Introduction of a factor, correcting for the deviation from that law, was found to be necessary. On the basis of this relation, extraction rates of solutes from capillaries can be determined if their diffusion coefficients are known.

The established relations between the diffusivity, the solute composition, and the diffusion rate are of practical value to the extraction and leaching operations. Their verification and further development are therefore recommended.

APPENDIX

1. Source and Quality of Chemicals Used

Commercially available materials were employed during present experimental work.

Sodium chloride, potassium sulfate, cupric sulfate pentahydrate, and sucrose were of a regular reagent grade quality.

Palmitic acid, practical, came from Matheson-Coleman and Bell Company. Source: animal fats; m.p. 59-61°C; composition by gas chromatography: 90% palmitic acid, 7.5% stearic acid, 1.0% myristic acid (C_{14} isomer, probably), 0.5% pentadecylic acid, and 0.01% margaric acid.

Tripalmitin, technical, supplied by Distillation Products Industries, a Division of Eastman-Kodak Company, was reported to contain from three to six percent of dipalmitin, and to have a melting point of 67-69°C.

Ursolic acid, crude grade, was bought from Bios Laboratories. Before its use in the experimental work, material was purified following procedure described by National Cranberry Association's Research Laboratory Report UN-3 1952. The melting point of purified product was determined at 286.5°C-288°C, which compares favorably with 285°C-288°C range quoted by literature (10).

Distilled water and methyl isobutyl ketone were used as solvents.

The distillation range of the latter was from 114.0°C to 116.5°C.

2. Physical Data

In the evaluation of experimental results, knowledge of the density of solutes, the solubility of solutes, and the density of solutions was necessary. Whenever possible, data from literature were utilized.

Density of palmitic acid, tripalmitin, and ursolic acid, not found in literature, was determined using Fryer and Weston method (A.O.C.S. Official Method Cc 10b-25, revised October, 1951) (22).

Solubility of ursolic acid, palmitic acid, tripalmitin, and of their mixtures in methyl isobutyl ketone was obtained by Reylly and Rae method (27). The same technique was used to estimate solubility of sodium chloride-sucrose and sodium chloride-potassium sulfate mixtures in water.

Density of saturated solutions was determined by means of the Mohr-Westphal balance (26).

Complete summary of physical data employed during the experimental work is given in Tables IX, X, XI, XII, and XIII.

Table IX

Density of Solutes

at 25°C

Solute	Density ρ_t (gm/cc)	Source
Cupric sulfate .5H_2O	2.286	(7)
Potassium sulfate	2.662	(7)
Sodium chloride	2.163	(7)
Sucrose	1.588	(7)
Palmitic acid	0.925	Experimental (Note 1)
Tripalmitin	0.922	-"-
Ursolic acid	0.969	-"-

Note 1. Determined by Fryer and Weston method (22)

Table X

Solubility of Solutes in Water

at 25°C

Solute	Composition (% by wt.)	Solubility C_s(gm/cc)	Source
Cupric sulfate .$5H_2O$	100	0.3128	(13)
Potassium sulfate	100	0.118	(20)
Sodium chloride	100	0.3171	(20)
Sucrose	100	0.9050	(20)
Sodium chloride -Potassium sulfate	50-50	0.398	Experimental (Note 1)
Sodium chloride -sucrose	25-75	1.136	-"-

Note 1. Determined by Reylly and Rae method (27).

Table XI

Solubility of Solutes in Methyl Isobutyl Ketone

at 25°C

Solute	Composition (% by wt.)	Solubility C_s(gm/cc)	Source
Palmitic acid	100	0.1124	Experimental (Note 1)
Tripalmitin	100	0.00448	-"-
Ursolic acid	100	0.00413	-"-
Palmitic acid -Tripalmitin	75-25	0.1070	-"-
-"-	50-50	0.1070	-"-
-"-	25-75	0.1070	-"-
Palmitic acid -Ursolic acid	50-50	0.0647	-"-
Tripalmitin -Ursolic acid	50-50	0.00995	-"-
Palmitic acid -Tripalmitin -Ursolic acid	33.3 -33.3 -33.3	0.0937	-"-

Note 1. Determined by Reylly and Rae method (27).

Table XII

Density of Saturated Solutions

at 25°C

Solvent : Water

Solute	Composition (% by wt.)	Density ρ_s (gm/cc)	Source
Cupric sulfate $.5H_2O$	100	1.211	(13)
Potassium sulfate	100	1.086	(20)
Sodium chloride	100	1.1978	(20)
Sucrose	100	1.3340	(20)
Sodium chloride -Potassium sulfate	50-50	1.249	Experimental (Note 1)
Sodium chloride -sucrose	25-75	1.445	-"-

Note 1. Determined on a Moor-Westphal balance (26).

Table XIII

Density of Saturated Solutions

at 25°C

Solvent : Methyl Isobutyl Ketone

Solute	Composition (% by wt.)	Density ρ_s (gm/cc)	Source
Palmitic acid	100	0.8072	Experimental (Note 1)
Tripalmitin	100	0.7976	-"-
Ursolic acid	100	0.7977	-"-
Palmitic acid -Tripalmitin	75-25	0.8071	-"-
-"-	50-50	0.8071	-"-
-"-	25-75	0.8071	-"-
Palmitic acid -Ursolic acid	50-50	0.8040	-"-
Tripalmitin -Ursolic acid	50-50	0.7983	-"-
Palmitic acid -Tripalmitin -Ursolic acid	33.3 -33.3 -33.3	0.8062	-"-

Note 1. Determined on a Moor-Westphal balance (26).

3. Sample Calculations

Sample Calculation # 1 - Diffusion coefficient of a single-component solute calculated from experimental data.

Basis : Run # 21c

Solute : Tripalmitin

Solvent : Methyl Isobutyl Ketone

Temperature : 25°C

Calculation of ρ_a and a

Data : $\rho_t = 0.922$ gm/cc

$\rho_s = 0.7976$ gm/cc

$C_s = 0.00448$ gm/cc

Capillary volume $V = 0.01735$ cc

Weight of total capillary loading $W = 0.01530$ gm

By material balance

$$\frac{W-W_s}{\rho_t} + \frac{W_s}{\rho_s} = V$$

Solving for W_s and substituting

$$W_s = \frac{\rho_t V - W}{\rho_t/\rho_s - 1} = \frac{(0.922)(0.01735)-(0.01530)}{0.922/0.7976-1} = 0.00439$$

Then fractions occupied by solid and saturated solution, are

$$V_s = W_s/\rho_s = 0.00439/0.7976 = 0.00550 \text{ cc}$$
$$V_t = W_t/\rho_t = 0.01091/0.922 = \underline{0.01185 \text{ cc}}$$
$$V = 0.01735 \text{ cc} \qquad \text{check}$$

and

$$\rho_a = W_t/V = 0.01091/0.01735 = 0.629$$
$$a = V_t/V = 0.01185/0.01735 = 0.683$$

Calculation of diffusion coefficient

Equation (12) is solved by trial and error using the following

data : $\rho_a = 0.629$

$a = 0.683$

$C_s = 0.00448$

$C_o = 0$

$\Delta C = C_s - C_o = 0.004488$

$$\sqrt{\pi}\left[\rho_a-(1-a)C_s\right] = \sqrt{\pi}\left[0.629-(1-0.683)(0.00448)\right] = 1.112$$

estimate $s = aC_s = (0.683)(0.00448) = 0.003054$

assume $M = 0.0665$

calculate $\dfrac{s}{M} = 0.04595$ $\qquad \dfrac{\Delta C - s}{M} = 0.02144$

obtain from the probability tables, Reference (14)

$$\therefore \psi\left(\frac{s}{M}\right) = 0.040752 \qquad \therefore \psi\left(\frac{\Delta C - s}{M}\right) = 0.018978$$

and substitute these values into Equation (12)

$$(0.040752) + (0.018978) = \frac{0.0665}{1.112} \text{ exp. } -(0.018978)^2$$

$$0.05973 \simeq 0.05975$$

Verify a, using Equation (8)

$$a = \frac{0.040752}{0.040752 + 0.018978} = 0.683$$

Get the relationship between x_s and t from Equation (6)

$$x_s = \frac{2\sqrt{D_e t}}{a}\psi\left(\frac{s}{M}\right) = \frac{2\sqrt{D_e t}}{0.683} (0.040723) = 0.1193 \sqrt{D_e t}$$

Solve for D_e, substituting values of x_s and t from Figure 6, Run # 21c; for instance

at $t = 4000$ min

$x_s = 0.139$ cm

$$D_e = \frac{(0.139 \text{ cm}/0.1193)^2}{(4000 \cdot 60)\text{sec.}} = 0.567 \times 10^{-5} \text{ sq.cm./sec.}$$

This is the diffusion coefficient of tripalmitin in methyl isobutyl ketone at 25°C calculated from experimental data.

Sample Calculation # 2 - Diffusion coefficient of a single-component solute calculated from empirical Wilke correlation (31)

Solute : Tripalmitin

Solvent : Methyl isobutyl ketone

Temperature : 25°C

Method involves application of the following equation

$$D_w = 7.4 \times 10^{-8} \frac{(x'M')^{0.5}(T)}{(\eta)\ (V')^{0.6}}$$

where

x'	=	1	association parameter of methyl isobutyl ketone
M'	=	100.16	molecular weight of methyl isobutyl ketone
η	=	0.538 cp.	viscosity of solution (in this case viscosity of pure solvent is taken due to small solubility of tripalmitin in methyl isobutyl ketone
T	=	298 °K	absolute temperature
V'	=	1189.4	molal volume of solute at normal boiling point, estimated from atomic volumes

substituting and solving

$$D_w = 7.4 \times 10^{-8} \frac{(1 \times 100.16)^{0.5}(298)}{(0.538)\ (1189.4)^{0.6}}$$

$$D_w = 0.586 \times 10^{-5}$$

Sample Calculation # 3 - Diffusion coefficient of a two-component solute calculated from experimental data

Basis : Run # 22b

Solute : Palmitic acid-Tripalmitin, a 50%-50% mixture by weight

Solvent : Methyl Isobutyl Ketone

Temperature : 25 ±0.011°C

Calculation of the effective interface concentration

Data :	for palmitic acid	C_{sA}	= 0.1124
		D_{eA}	= 1.110×10^{-5}
		W_A	= 256.42
	for tripalmitin	C_{sB}	= 0.00448
		D_{eB}	= 0.567×10^{-5}
		W_B	= 807.29
	for 50%-50% mixture by weight	C_{sM}	= 0.1070

Relative diffusion rate of palmitic acid to that of tripalmitin is determined from Equation (16)

$$\frac{N_A}{N_B} = \frac{(1.11\times10^{-5})(0.1124/256.42)}{(0.567\times10^{-5})(0.00448/807.29)} = 154.7 \Big/ 1$$

Next, from composition of solute in the solute bed,

palmitic acid	50% wt./256.42	=	0.195 moles	75.9% mole
tripalmitin	50% wt./807.29	=	0.062 "	24.1% "
	100% wt.		0.257 moles →	100.0% mole

effective composition of solid solute at the interface is estimated

palmitic acid	50% wt.	x 1	=	0.5 gm	0.64% wt.
tripalmitin	50% wt.	x 154.7	=	77.35 gm	99.36% wt.
	100% wt.			77.85 gm →	100.0 % wt.

from which effective interface concentration of solute in solution is obtained from Equation (18)

$$C'_{sm} = (C_{sA}n_A + C_{sB}n_B)\left(\frac{C_{sM}}{C_{sA}+C_{sB}}\right)$$

$$= (0.1124 \times 0.0064 + 0.00448 \times 0.9936)\left(\frac{0.1070}{0.1124+0.00448}\right)$$

$$= 0.00474$$

Calculation of ρ_a and a

Data : $\rho_t = (0.925)(0.50) + (0.922)(0.50) = 0.924$

$\rho_s = 0.8071$

$V = 0.03052$

$W = 0.02780$

By material balance

$$\frac{W - W_s}{\rho_t} + \frac{W_s}{\rho_s} = V$$

Solving for W_s and substituting

$$W_s = \frac{\rho_t V - W}{\rho_t / \rho_s - 1}$$

$$= \frac{(0.924)(0.03052) - (0.02780)}{0.924/0.8071 - 1}$$

$$= 0.00276$$

Then fraction occupied by solid and saturated solution, are

$$V_s = W_s / \rho_s = 0.00276 / 0.8071 = 0.00342 \text{ cc}$$

$$V_t = W_t / \rho_t = 0.02504 / 0.924 = \underline{0.02710 \text{ cc}}$$

$$V = 0.03052 \text{ cc}$$

and

$$\rho_s = V_t / V = 0.00504 / 0.03052 = 0.[illegible]$$

$$\varepsilon = V_t / V = 0.02710 / 0.03052 = 0.[illegible]$$

Calculation of diffusion coefficient

Equation (12) is solved by trial and error

Data :

$$\rho_a = 0.820$$

$$a = 0.889$$

$$C'_{sm} = 0.00474$$

$$C_o = 0$$

$$\Delta C = C'_{sm} - C_o = 0.00474$$

$$\sqrt{\pi}\left[\rho_a - (1-a)C'_{sm}\right] = \sqrt{\pi}\left[0.820 - (1-0.889)(0.00474)\right] = 1.450$$

estimate $s = aC'_{sm} = (0.889)(0.00474) = 0.00421$

assume $M = 0.078$

calculate $\dfrac{s}{M} = 0.0541 \qquad \dfrac{\Delta C - s}{M} = 0.00667$

obtain from probability tables, Reference (14)

$$\therefore \psi\left(\frac{s}{M}\right) = 0.04796 \qquad \therefore \psi\left(\frac{\Delta C - s}{M}\right) = 0.00591$$

and substitute these values into Equation (12)

$$(0.04796) + (0.00591) = \frac{0.0780}{1.450} \text{ exp. } -(0.00591)^2$$

$$0.05387 \simeq 0.05380$$

Verify a , using Equation (8)

$$a = \frac{0.04796}{0.04796 + 0.00591} = 0.890$$

Get desired relationship between x_s and t from Equation (6)

$$x_s = \frac{2\sqrt{Dt}}{a} \psi\left(\frac{s}{M}\right)$$

$$= \frac{2\sqrt{Dt}}{0.889} (0.04796)$$

$$= 0.1078 \sqrt{Dt}$$

Solve for D_e , substituting values of x_s and t from Figure 7, (Run # 22b)

e.g. at $t = 2000$ min.

$x_s = 0.115$ cm.

and

$$D_e = \frac{(0.115 \text{ cm.} / 0.1078)^2}{(2000 \times 60) \text{ sec.}}$$

$$= 0.950 \times 10^{-5} \text{ sq.cm./sec.}$$

This is the diffusion coefficient of a 50%-50% by weight mixture of palmitic acid - tripalmitin calculated from experimental data.

Sample Calculation # 4 - Deviation from Fick's Law estimated from experimental extraction rate data

Basis : Run # 11a

Solute : Sodium chloride

Solvent : Water

Calculation of diffusion coefficient from Equation (15), assuming quasi-steady-state conditions (Ref.17)

$$N_e = D_f \left(\frac{\Delta C}{x_{av}} \right) \tag{15}$$

Data :

$\rho_a = 1.397$

$a = 0.645$

$x_{av} = 0.5 \pm 0.5$ cm.

$t = 2200$ min. (from Figure 5)

If total solute extracted from initial solute bed in the capillary is expressed by

$$P = (a)(\rho_t) + (1-a)(C_s)$$

$$= (0.645)(2.163) + (0.355)(0.3171)$$

$$= 1.508 \text{ gm./cc.}$$

then experimental diffusion rate N_e, assuming 1 sq.cm. cross-sectional area, equals

$$N_e = \frac{(1.508)\ \text{gm./cc.}\ (1.0)\ \text{cc./sq.cm.}}{(2200 \times 60)\ \text{sec.}}$$

$$= 1.143 \times 10^{-5}\ \text{gm./sq.cm.-sec.}$$

Substituting this value into Equation (15) and solving for D_f, the apparent diffusion coefficient is obtained

$$D_f = N_e \left(\frac{x_{av}}{\Delta C} \right)$$

$$= (1.143 \times 10^{-5})\ \text{gm./sq.cm.-sec.} \quad \frac{(0.5)\ \text{cm.}}{(0.3171)\ \text{gm./cc.}}$$

$$= 1.802 \times 10^{-5}\ \text{sq.cm./sec.}$$

Since actual diffusion coefficients

$$D_e = 1.534 \times 10^{-5}$$

the deviation from Fick's Law becomes

$$\frac{D_f - D_e}{D_e} = \frac{1.802 - 1.534}{1.534} = 0.176 = 17.6\%$$

This deviation, found to be a function of solubility, is plotted in Figure 16, and from the slope of the line the following relation established

$$\frac{D_f - D_e}{D_e} = C_s^{1.6}$$

from which generalized factor correcting for deviation from Fick's Law becomes

$$\Phi_L = (1 + c_s^{1.6})$$

Applying this factor to the Fick's First Law equation, the desired relationship between the experimental diffusion coefficient D_e, and the actual diffusion rate N_e, for a solute diffusing from a solid-liquid interface, is obtained

$$N_o = D_f \left(\frac{\Delta C}{x_{av}} \right)$$

$$= D_e \left(\frac{\Delta C}{x_{av}} \right) \Phi_L$$

$$= D_e \left(\frac{\Delta C}{x_{av}} \right) \quad (1 + c_s^{1.6})$$

NOMENCLATURE

a	- fractional volume of solid solute in solute bed
A, B	- single-component solutes
b	- distance, cm.
C	- concentration of solution, gm./cc.
C_o	- concentration at the capillary entrance, gm./cc.
C_s	- solubility, or concentration of a single-component solute at the interface, gm./cc.
C_{sM}	- solubility of a mixed solute, gm./cc.
C'_{sm}	- effective interface concentration of a mixed solute, in solution, gm./cc.
ΔC	- concentration driving force between interface and capillary entrance, gm./cc.
$(\partial C/\partial x)_i$	- concentration gradient at interface in straight capillary, gm./cc./cm.
D	- diffusion coefficient, sq.cm./sec.
D_e	- diffusion coefficient determined from experimental data, sq.cm./sec.
D_f	- diffusion coefficient estimated from experimental extraction rate data using Fick's First Law Equation
D_r	- diffusion coefficient from literature reported by various investigators, sq.cm./sec.
D_s	- diffusion coefficient of a mixed solute estimated from straight line relation between diffusivity and solute composition, sq.cm./sec.
D_w	- diffusion coefficient estimated from empirical Wilke (31) correlation, sq.cm./sec.
m	- multi-component solute
M	- concentration constant in two-phase capillary equation

n	- weight fraction
n_A, n_B	- weight fractions of components A and B in mixed solute
N	- rate of solute leaving interface by diffusion, gm./sq.cm.-sec.
N_A, N_B	- diffusion rate of components A and B, gm./sq.cm.-sec.
N_e	- experimental diffusion rate, gm./sq.cm.-sec.
P	- total solute extracted from initial solute bed in the capillary, gm. solute/cc. of solute bed
s	- point of inflection constant of two-phase capillary equation
t	- time, sec.
T	- absolute temperature, °K
v	- velocity of solvent at any point in diffusion path relative to capillary wall, cm./sec.
V	- total capillary volume, cc.
V_s	- volume of capillary occupied by saturated solution, cc.
V_t	- volume of capillary occupied by solid solute, cc.
V'	- molal volume of solute at normal boiling point, cc./gm.mole
W	- total weight of solid solute and of saturated solution in the capillary, gm.
W_s	- weight of saturated solution in the capillary, gm.
W_t	- weight of solid solute in the capillary, gm.
x	- distance, cm.
x_{av}	- average distance from interface to capillary entrance through which solute diffused during the extraction, cm.
x_s	- distance from capillary entrance to interface, cm.
x'	- association parameter of solvent

y_o - mole fraction of vapor at liquid interface in an evaporating system

- viscosity of solvent, cp.

ρ_a - apparent density of solute bed, gm./cc.

ρ_s - density of saturated solution, gm./cc.

ρ_t - density of solid solute, gm./cc.

ϕ_L - factor correcting for deviation from Fick's First Law in solid-liquid systems

ϕ_V - factor correcting for deviation from Fick's Second Law in liquid-vapor systems (1, 3)

ψ - inverse error function

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