

單分子層內的 表面擴散 (I)

鄭 盛 澤*

Surface Diffusion in Monomolecular films (I)

*Sung T. Chung · **John C. Berg

*Dept. of Poly. Sci. & Tech., College of Eng., Inha Univ.

**Dept. of Chem., Univ. of Washington, Seattle

Abstract

Experimental data on surface diffusion coefficients are obtained for monolayers of myristic, pentadecylic, palmitic, stearic and oleic acids formed on 0.01N HCl aqueous substrates at 22.3°C using a radioactive tracer technique. Each of these acids is studied at various monolayer concentrations with reference to surface pressure-area isotherms.

Introduction

The presence of surface active substances exerts a significant influence, as is well known, on the motion of fluid interfaces¹⁾. A detailed hydroynamical treatment of such interfacial effects, collectively known as the Marangoni effect, requires in part a knowledge on the surface diffusion of the material. The possible importance of surface diffusion in fluid capillary systems, in particular involving insoluble monolayers, was suggested by Levich,¹¹⁾ Whitaker,¹⁴⁾ and Berg and Acrivos.³⁾ Surface diffusion in an insoluble monolayer may also be an important process in studies of kinetics of interfacial reactions between two components of a monolayer, as suggested by Gaines.⁶⁾

The review of the previous literature, as summarized in Table 1, reveals that the experimental systems thus far studied are relatively scattered as well as scant in number. Actually there are not

many types of surfactants convenient for direct study because of their appreciable transfer into the adjacent bulk phases. The homologous series of long chain fatty acids from myristic acid to stearic acid as well as oleic acid in their various monolayer states can be studied systematically to provide a further indication of the order of magnitude of the surface diffusivity with reference to the molecular structure of insoluble monolayers. This paper deals with the experimentation and the next with the theory.

Table 1. Summary of Experimental Surface Diffusion Coefficients at 22°C

Investigators	Types of Film	Ds (cm ² /sec)
Imahori ⁹⁾	Gaseous Protein in castor oil film	1.1×10 ⁻⁶
Mass ¹²⁾	Condensed Calcium Palmitate and stearate	1×10 ⁻⁷
Sakata and Berg ¹³⁾	Intermediate myristic acid	3×10 ⁻⁵
	Liquid-expanded myristic acid	3×10 ⁻⁴

*仁荷大學 高分子工學科

**Dept. of Chem. Eng., Univ. of Washington

Experimentation

To measure the surface diffusivity the method of measuring surface concentration had to be chosen first. The radioactive tracer technique that had been used by the previous workers was employed. The surface of a Langmuir trough was initially divided into two equal compartments by a barrier of some appropriate material. An ordinary film and a tagged film of the same material were then spread separately on the two sides of the dividing barrier. After the adjustment was made for the overall uniform concentration and hence for the equal surface pressures on both sides, the barrier was lifted. There would be counterdiffusion of the ordinary film and the tagged film. Since the overall surface pressure would be maintained uniform throughout the experiment because of the uniform rates of film loss over the entire surface, there would be no occurrence of monolayer

flow. The extent of diffusion was determined by measuring the surface radioactivity of the tagged film as it diffused into the ordinary film with a radiation detector. The resulting unsteady-state surface profiles were then analyzed with an appropriate experimental model for surface diffusion with allowance for the effect of any film loss through the bulk phases on the overall mass transfer of the film loss through the bulk phases on the overall mass transfer of the film. The surface diffusion coefficients thus determined were the average values over the surface concentration ranges during surface diffusion runs.

The experiments with extremely small amounts of film material (less than 10^{-4} g) required scrupulous care for cleanliness of all apparatus and glassware coming in contact with the substrate solution and the spreading solution. In surface diffusion experiments great pains had also to be taken to produce convection-free runs for long periods of time.

Apparatus

The apparatus is shown schematically in Fig. 1. The trough was milled from a slab of $\frac{1}{2}$ in. thick polypropylene, and its inside dimensions were $43 \times 5.5 \times 0.16$ cm. It was made as shallow as possible to exclude the possibility that convection currents would occur in the substrate. The movable barriers, which were used to confine and adjust the film area, were cut from Teflon slabs into sticks of $11.6 \times 1.3 \times 0.7$ cm. The barrier advancing assembly with a pair of forks was designed to compress or dilate the film with precision in the course of equating the initially often unbalanced surface pressures of the two films. A Teflon strip was used as a divider of the surface of the trough and also as a sensitive means of detecting unbalanced surface pressures. It was cut from a piece of 0.03 in. thick Teflon tape into a 0.2 mm wide strip. Such a thin Teflon strip was quite convenient to use because of its hydrophobic and flexible property. A lifting device and a Teflon-made guard were designed for the thin flexible Teflon barrier to prevent any deep mixing of the contingent films in the lifting stage and any film leakage past the barrier that can occur when the

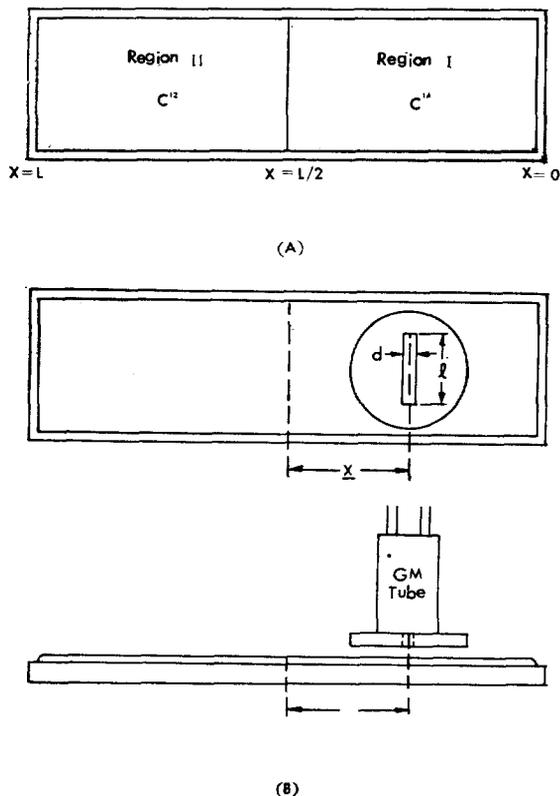


Fig. 1. Schematic diagram of an apparatus

barrier becomes taught.

Surface radioactivity was measured with a thin end window G-M tube, Amperex Type 200 LB, connected to a Nuclear-Chicago Model 186A Scalar. It had a window thickness of 5 microns (1.4 mg/cm^2) and an effective window diameter of 2.5 cm, with a transmission of approximately 40% at 50 KeV (the average energy of carbon-14 beta rays). The G-M counter was chosen in this work among other detectors, such as scintillation counter and proportional counter, because of the stability of the counting system and the simplicity of the electronics involved. The G-M tube was mounted in a carriage which could be moved along the length of the trough on runners. The tube could also be moved vertically by means of a vernier, allowing the detector to be placed at any desired height above the surface film.

Since the radioactive source was carbon-14, an emitter of low energy beta rays, it was necessary to assess the average concentration of a tagged substance in a large enough sampling area under the counter. This was achieved by placing a slitted cap at the end of the detector, so that the surface activity at any position along the length of the trough could be measured. It was made from a 3 mm thick piece of Plexiglas with a 3 mm wide by 4.5 cm long slit. It would have been necessary to correct for the variation of surface activity across the width of the slit if the counting rate were extremely low, the width of the slit were large, the thickness of the cap were small, or the height of the cap from the surface were large, since each of these factors would tend to increase the "view" of the surface as seen by the G-M tube. However, with the physical dimensions involved in this experiment, the variation of surface activity across the slit could be neglected.

The carriage assembly and the trough were enclosed inside cover to eliminate air currents and minimize evaporation. Water wicks were also placed inside the cover to reduce evaporation and to provide a saturated atmosphere. The cover was a double-walled Plexiglas box through which thermostat water could be circulated to maintain the environment of the film at any temperature ranging from 10°C to 40°C . The

trough was arranged inside the cover such that, separated from the other major components of the equipment, it was possible to prevent any mechanical disturbances made during the course of scanning the surface with the radiation detector from transmitting directly from the box to the trough except through the counting table. The counting table was specially constructed to reduce the building vibrations and successful runs could be achieved even at surface pressures less than 0.5 dynes/cm . The Gilmon micrometer burets, 0.2 ml in capacity, were used to deliver separately the spreading solutions of the ordinary film and the tagged film onto the substrates.

Operating Procedure

All apparatus and glassware coming in contact with either the substrate solution or the spreading solution were cleaned carefully before each experimental run in accordance with the procedure that was developed satisfactorily in other types of monolayer experiments.⁶⁾

The substrate was poured into the trough to a depth of 3 mm, providing a positive meniscus around the trough. The movable Teflon barriers were swept across the surface to provide a clean surface, and were positioned at the ends of the trough. In placing next the surface-dividing barrier across the trough, the parts of the barrier lying on the top edges of the trough were first affixed with petroleum jelly and a small wedge-shaped Teflon piece at each intersection of the barrier and the inside edge of the trough to block the whole. By pulling the end of the barrier toward the outside, it was made to lie on the surface in a nearly straight line.

Spreading solutions of the tagged film and the ordinary film were delivered onto the surface by two micrometer burets. When two films were formed one by one on their surfaces, the barrier guard played the important role in protecting the surface-dividing barrier against the highly unbalanced surface pressures that were caused before one of the films was not yet spread. The barrier remained in the shape of a straight line (cf. Figure 2a). As could be expected from spreading the films separately, the surface

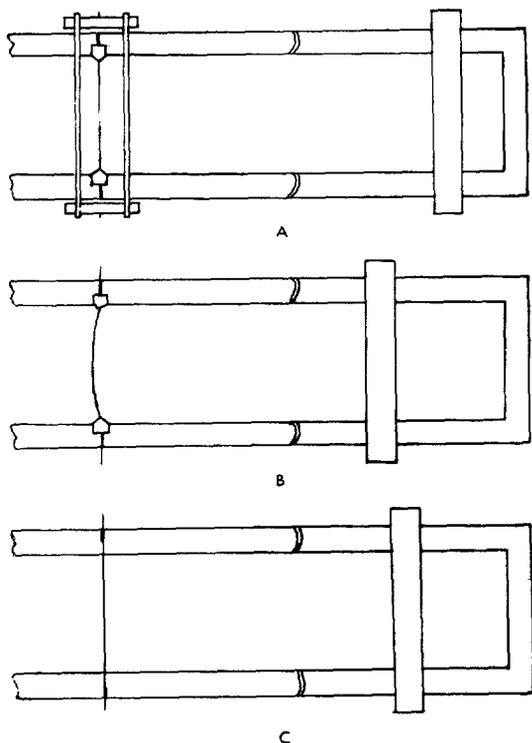


Fig. 2. Procedures of equating surface pressures

pressures on the two sides were not exactly balanced. Since the difference between them was sometimes large, a preliminary adjustment was made before the guard was taken away by distending or compressing the ordinary film with the movable barrier held in the forks by a distance calculated on the basis of the known amounts spread. Under favorable conditions such a preliminary adjustment could achieve equal uniform surface pressure on both sides of the barrier. More often, however, the dividing barrier still bowed out slightly toward the side of higher surface pressure after the guard was taken away (cf. Figure 2b). Such a remaining imbalance would usually arise not because of likely errors in film spreading with the burets, but because the concentration of the spreading solution of the tagged film was usually not known with complete accuracy. Final adjustment was then made by further manipulating the ordinary film, and the total distance moved by the barrier was recorded to calculate the overall uniform concentration on the surface (cf. Figure 2c).

Soon after the surface pressures of the two films were equalized, the G-M tube was moved very slowly to determine the surface activities at about 15 points at intervals of 0.5 cm. At each point the surface radioactivity was measured for two minutes. The reference time was set when the G-M tube was positioned at the site of the dividing barrier, and the actual time lag (~ 20 minutes) could be accepted in this work because the rate of surface diffusion was sufficiently low.

The radioactive materials were supplied in benzene solution in Pyrex glass ampoules. As a spreading solvent, n-hexane was chosen because of its superiority to benzene as discussed in the literature.^{2,5)} The spreading solutions of the radioactive and the non-radioactive material for a given surfactant was prepared to have initially about the same concentrations. The concentrations varied from 0.1 mg of surfactant per ml of solution to 0.2 mg/ml, depending on the radioactivity of the supplied radioactive material, to produce a desirable initial film coverage ($20\text{--}50 \text{ \AA}^2/\text{molecule}$) on a $5.5 \text{ cm} \times 19 \text{ cm}$ surface by delivering about 0.03 ml of the solution with a 0.2 ml capacity micrometer buret.

Systems Studied

This work dealt with the homologous series of

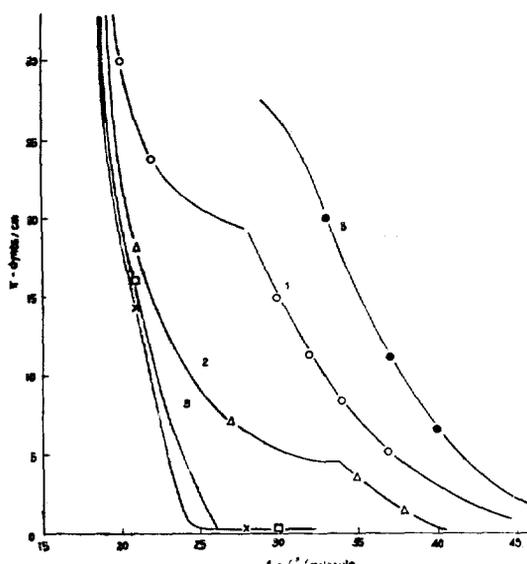


Fig. 3. Initial surface concentrations marked

saturated long chain fatty acids-myristic acid, pentadecylic acid, palmitic acid and stearic acid as well as oleic acid. Each of these acids was studied at various monolayer concentrations with reference to the π -A curves, as shown in Figure 3. The duration of the surface diffusion process was limited so that monomolecular film did not undergo any two-dimensional phase transition owing to the loss of film molecules through the adjacent bulk phases (primarily, desorption into the substrate).

Monolayers were all spread on 0.01N HCl aqueous solutions. This acidic substrate has been used in the acquisition of surface isotherms and has proved to retard significantly the rate of film desorption into the subphase. All measurements were made at room temperature (22.3°C). With water circulating through the thermostat, the variation of temperature in the course of one experimental run never exceeded more

Data analysis

Monolayer Concentration vs. Counting Rate With the radioactive tracer technique monolayer concentrations on the surface were determined in terms of radiation counting rates. They were related to each other by the equation of Aniansson:¹⁾

$$\Gamma = \frac{a_s}{SA} \quad (1)$$

where

a_s =activity from surface layer in counts per minute,
 A =area as viewed by a radiation counter,
 S =specific activity i.e., activity in counts per minute per mole of the radioactive substance.

The dimensionless monlayer concentrations were then calculated by the simple relationship:

Table 2. Fatty Acids-¹⁴C

Compounds	Radioactivity mc/mM	Packaging	Vendors
Myristic acid	15.4	50 μ c in 0.6 ml Benzene solution	Amersham/Searle Corp., Des Plaines, Ill.
Pentadecylic acid	57.5	50 μ c in 0.2 ml Benzene solution	Dohm Products, Ltd., North Hollywood, Calif.
Palmitic acid	55.2	50 μ c in 0.6 ml Benzene solution	Amersham/Searle Corp.
Stearic acid	48.4	50 μ c in 0.6 ml Benzene solution	Amerhsam/Searle Corp.
Oleic acid	57.8	50 μ c in 0.6 ml Benzene solution	Amersham/Searle Corp.

than $\pm 0.2^\circ\text{C}$.

The carbon-12 ordinary and carbon-14 tagged acids were used as they were supplied in the highly purified state (99+mole%). The normal myristic, palmitic, stearic and oleic acids were obtained from the Nutritional Biochemicals Corporation of Cleveland, Ohio and pentadecylic acid was supplied by the Applied Science Laboratory, Inc. of State College, Pennsylvania. Detailed information on the radioactive acids used is given in Table 2.

N-hexance spreading solvent was Phillips 66 pure grade of 99 mole % purity. Hydrochloric acid to adjust the acidity of substrate, and other chemicals, such as potassium permanganate, sodium hydroxide, sulfuric acid, potassium dichromate and syrupy phosphoric acid used in preparing the purified water and cleaning the equipment were all reagent grade.

$$\frac{\Gamma}{\Gamma_0} = \frac{a_s}{a_{s0}} \quad (2)$$

Related to the problem of monlayer desorption into the underlying liquid would be that of backscattering, the contribution to the surface counts by the desorbed molecules, that is,

$$\frac{\Gamma}{\Gamma_0} = \frac{a_s - a_b}{a_{s0}} \quad (3)$$

This correction proved to be unnecessary, however, because of the relatively low concentration of desorbed acid in the substrate, the short range of the low-energy beta-rays of carbon-14, and the degradation in energy by the substrate. An approximate calculation for the maximum backscattering contribution shows that the correction term is less than 5%. This was

also confirmed experimentally by sweeping the surface clean of the monolayer and measuring the activity of the monolayer-free surface. The counting rate was substantially the same as the background count.

Evaluation of D_s An appropriate model for the calculation of surface diffusion coefficients from the unsteady-state surface concentration profiles was developed by Sakata and Berg¹³⁾ in the analysis of their measurements with monolayers of myristic acid. Their model was slightly modified in this work.

Although the monolayers studied in this work had very small vapor pressures, the transfer of film molecules into the gas phase was concurrently taking place with desorption into the substrate. This additional contribution to the overall film loss had to be taken into account. It was done simply by characterizing the kinetics of the overall film loss by a single rate constant on the basis of a first-order linear kinetics.

$$-\left(\frac{d\Gamma}{dt}\right)_{\text{overall}} = \kappa_{\text{overall}}\Gamma \quad (4)$$

Associated with the initial condition, the time course is described by

$$\frac{\Gamma}{\Gamma_0} = \exp(-\kappa_{\text{overall}} t) \quad (5)$$

It should be indicated that the rate constant, κ_{overall} calculated by Equation (5) from the experimental data represents the "net" rate of the overall film loss.

By the use of Equation (4), the experimentally determined unsteady-state surface concentration profiles for one-dimensional surface diffusion are described by the following single differential equation:

$$\frac{\partial \Gamma}{\partial t} = D_s \left(\frac{\partial^2 \Gamma}{\partial x^2} \right) - \kappa_{\text{overall}} \Gamma \quad (6)$$

assuming D_s to be independent of surface concentration. This equation was solved numerically for (t, x) with the associated no-flux boundary conditions and the experimentally determined initial conditions. The step-change profile should not be used as the initial condition because the actual initial profile may differ

somewhat from it. In this connection, it should be noted that the experimental data on D_s reported by the previous workers who used the step-change initial condition would be somewhat larger than the true values. The numerical solution was obtained using a central difference formula for the $\frac{\partial^2 \Gamma}{\partial x^2}$ term and a forward difference formula for the $\frac{\partial \Gamma}{\partial t}$ term, with the choice of 0.5 cm and one minute for the distance and time intervals, respectively. The computation was carried out by a CDC 6400 digital computer. The best fit of the data on D_s was determined by the method of least squares.

Results and Discussion

Film Loss Experimental plots of $\ln \Gamma/\Gamma_0$ vs. t for monolayers of myristic acid studied are given in Figure 4. The straight lines are drawn through the experimental points. The values of κ_{overall} obtained from the slopes are summarized in Table 3. Since the experiments were conducted at constant surface areas for the long periods of time, these values represent the average values over the range of surface concentrations that changed during the course of runs.

The experimental data lead to the following observations:

- (1) The loss rate constants are relatively constant

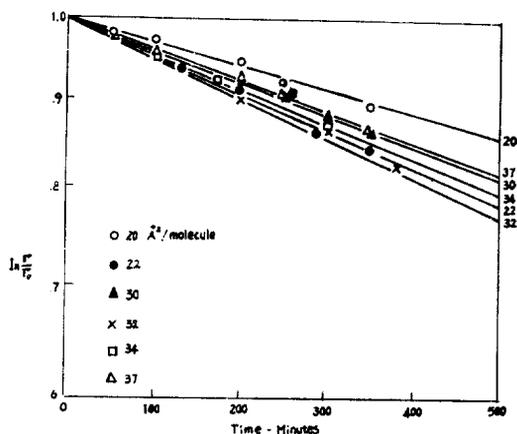


Fig. 4. Loss of myristic acid monolayer

- with surface concentration in fluid monolayer states, but are much smaller in condensed states.
- (2) The rate constants decrease with increased chain length.
 - (3) Oleic acid, which has a double bond in the chain, has a smaller rate constant than stearic acid, and its rate constant is comparable to that of palmitic acid which is shorter than oleic acid by two carbon atoms.
 - (4) The rate of film loss is apparently smaller than that predicted by the diffusion of film through the substrate.

These observations are consistent with the idea that the rate of film loss in the C_{14} to C_{18} range is controlled primarily by the presence of an energy barrier. From the absolute theory of rate processes,⁷⁾

$$\kappa_{\text{overall}} = \frac{KT}{h} \exp(-\Delta G_{\text{overall}}/KT) \quad (7)$$

where $\Delta G_{\text{overall}}$ is the free energy of activation for overall film loss by desorption and evaporation. $\Delta G_{\text{overall}}$ is only a weak increasing function of surface pressure (surface concentration).

No one has reported the rates of film loss for the fatty acids studied except for myristic acid. It is only possible, therefore, to check the reliability of the data obtained on a limited basis, i. e., by com-

Table 3. Experimental Overall Rate Constants of Film Loss

Substances	A, Å ² /molecule	κ_{overall} , min ⁻¹
Myristic acid	20	3.330×10^{-4}
	22	4.507×10^{-4}
	30	4.463×10^{-4}
	32	4.588×10^{-4}
	34	4.091×10^{-4}
	37	3.993×10^{-4}
Pentadecylic acid	21	~0
	27	1.547×10^{-4}
	35	1.473×10^{-4}
	38	1.581×10^{-4}
Palmitic acid	21	~0
	30	6.092×10^{-5}
Stearic acid	21	~0
	28	5.011×10^{-5}
Oleic acid	33	1.480×10^{-4}
	37	1.481×10^{-4}
	40	1.480×10^{-4}

paring only the results of myristic acid with those obtained by the previous workers. Comparing the present results (~0.043 % per minute) with them, the present ones are very close to those of Sakata and Berg (~0.05 % per minute). These results are significantly lower than those obtained by Saraga (~0.1 % per minute).¹⁵⁾

Surface Diffusion Typical unsteady-state surface concentration profiles obtained are presented in Figure 5. The solid lines represent the solutions to Equation (6), using in each case, the values of D_s which produced the best fit of the data (Table 4).

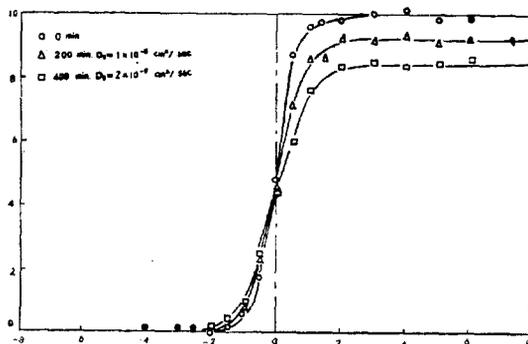


Fig. 5. Surface concentration profile of myristic acid for $A=34 \text{ \AA}^2/\text{molecule}$

During the course of a diffusion run, the concentration level of tagged monolayer on the right hand side of the profile dropped with time because of the loss of molecules from the monolayer. The overall monolayer concentration, however, remained uniform across the surface, as contrasted to surface flow experiments.

In the course of obtaining the present results, great pains were taken to produce convection-free runs. When runs were made in a constant temperature chamber on the counting table built up within a vibration-free room, the erratic distribution of surface counts, as observed by Mass,¹²⁾ was seldom displayed. The thin elastic Teflon surface-dividing barrier, the lifting device and the barrier guard played an important role in preventing the occurrence of surface convection.

Comparison of the data on D_s of myristic acid with those of Sakata and Berg¹³⁾ indicates that the present data are about one order of magnitude smaller than theirs. As mentioned earlier, such a discrepancy may be attributed primarily to their inappropriate use of step-change profiles as the initial conditions in their fit of the data.

It may be safe to believe that the present data approach the true values within an order of magnitude. Further refinement of these data is not possible because of statistical errors contained in the measurements of surface activities due to the inherent nature of nuclear disintegrations, relative insensitivity of the variation in profiles with respect to the values for D_s , and the geometrical arrangement of the counting system which has a smoothing-effect on the observed concentration gradients.

Table 4. Experimental Surface Diffusion Coefficients

Substance	A, Å ² /molecule	Film State	D_s Average cm ² /sec
Myristic acid	20	Condensed	1×10^{-7}
	22	Intermediate	8×10^{-6}
	30	Expanded	2×10^{-5}
	32	Expanded	1×10^{-5}
	34	Expanded	1×10^{-5}
	37	Expanded	3×10^{-5}
Pentadecylic acid	21	Condensed	1×10^{-7}
	27	Intermediate	3×10^{-6}
	35	Expanded	1×10^{-5}
	38	Expanded	8×10^{-6}
Palmitic acid	21	Condensed	1×10^{-7}
	30	Condensed-gaseous	5×10^{-6}
Stearic acid	21	Condensed	1×10^{-7}
	28	Condensed-gaseous	5×10^{-6}
Oleic acid	33	Expanded	7×10^{-6}
	37	Expanded	9×10^{-6}
	40	Expanded	6×10^{-6}

Conclusions

Molecular migration in monolayers of myristic, pentadecylic, palmitic, stearic and oleic acids on 0.01N HCl aqueous substrates at 22.3°C was studied with a radioactive tracer technique. A two-dimensional form of Fick's equation with a modification to account for

the loss of film molecules through the adjacent bulk phases was used to calculate the experimental surface diffusion coefficients from the unsteady-state surface concentration profiles. The data indicated the following:

(i) The surface diffusivity was weakly dependent on surface concentration within an expanded phase. For myristic acid, $D_s \sim 1-3 \times 10^{-5}$ cm²/sec; for pentadecylic acid, $D_s \sim 0.8-1 \times 10^{-5}$ cm²/sec; for oleic acid, $D_s \sim 0.6-1 \times 10^{-5}$ cm²/sec.

(ii) The surface diffusivity in the intermediate phase was smaller than in the expanded phase, but the difference was within one order of magnitude. For myristic acid, $D_s \sim 8 \times 10^5$ cm²/sec; for pentadecylic acid, $D_s \sim 3 \times 10^{-6}$ cm²/sec.

(iii) The surface diffusivity in the condensed state was smaller by nearly two orders of magnitude than in the gas-solid transition state. In the condensed state, $D_s \sim 1 \times 10^{-7}$ cm²/sec for all acids; in the gas-solid transition states, $D_s \sim 1 \times 10^{-6}$ cm²/sec for stearic acid and $D_s \sim 5 \times 10^{-6}$ cm²/sec for palmitic acid.

(iv) The surface diffusivity did not vary simply with the chain length at a given concentration. It depended on the phase which it exhibited at such a concentration. In the same film state the greater chain length led to the smaller values for D_s .

Acknowledgement

The authors gratefully acknowledge the financial assistance of the Office of Saline Water, U.S. Department of the Interior.

Literature Cited

1. Aniansson, G., *J. Phys. Chem.*, **55**, 1286 (1951).
2. Archer, R. J., and La Mer, V. K., *J. Phys. Chem.*, **59**, 200 (1955).
3. Berg, J. C., and Acrivos, A., *Chem. Eng. Sci.*, **20**, 737 (1965).
4. Chung, S. T., *J. KICChE*, **10**, 43 (1972).
5. Cook, H. D., and Ries, H. E., Jr., *J. Phys. Chem.*, **60**, 1533 (1956).
6. Gaines, G. L., Jr., *Insoluble Monolayers at*

- Liquid-Gas Interface*, p. 304, Interscience, New York, 1966.
7. Glasstone, S., Laidler, K., and Eyring, H., *The Theory of Rate Processes*, McGraw-Hill, 1941.
 8. Harkins, W.D., *The Physical Chemistry of Surface Films*, Reinhold, New York, 1952.
 9. Imahori, K., *Bull. of Chem. Soc. of Japan*, **25**, 13 (1952).
 10. Lim, Y.C., Ph.D. Thesis, University of Washington, 1971.
 11. Levich, V.G., *Physicochemical Hydrodynamics*, Prentice Hall, New Jersey, 1962.
 12. Mass, R.O., M.S. Thesis, University of Illinois, 1964.
 13. Sakata, E.K., and Berg, J.C., *Ind. Eng. Chem., Fund.*, **8**, 570 (1969).
 14. Whitaker, S., *Ind. Eng. Chem., Fund.*, **3**, 132 (1964).
 15. Ter Minassian-Saraga, *J. Colloid Sci.*, **11**, 398 (1956).

