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Chemical Reactions in Monolayer Films. Chromatography, a Multicompartment Trough, and the Hydrolysis of Surfactant Ester Derivatives of Tris(2,2′-bipyridine)ruthenium(II)$^{2+}$

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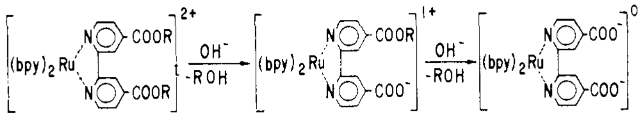
Abstract: There is renewed interest in studying chemical reactions of surfactant molecules in monolayer arrays at the air-water interface. High-performance liquid chromatography and vapor-phase chromatography have been used for the first time to detect, quantitate, and help characterize the small amounts of material contained in such surface films, ca. 10^{-9}-10^{-10} mol/cm^2. A multicompartment trough has been designed and used to allow a series of chemical reactions to be performed upon a well-defined monolayer film. The alkaline hydrolysis of $\{(bpy)_2Ru^{II}[bpy(COOR)_2]\}^{2+}$ in monolayer films ($R = C_{18}H_{37}$) is found to proceed more rapidly than in homogeneous, aqueous solution ($R = C_2H_5$) at the same bulk pH. Monitoring the stability of surface films and their hydrolytic reactions by chromatography has proven superior to observing area changes at constant surface pressure.

There is renewed interest in studying chemical reactions of surfactant molecules in monolayer assemblies. Use has been made of the high concentration of reactive functionalities constrained in a single plane to produce reaction products and kinetics different from what are observed in homogeneous solution[1,2] or to achieve ultrathin, oriented polymer films.[3-7] The detection and measurement of chemical reaction in monolayers has been generally carried out with the same tools that are used to study the properties of the monolayer itself: e.g., surface area-pressure isotherms, surface potential, and surface viscosity.[8] However, the variation of monolayer composition and identification of new products cannot be directly obtained from such measurements. When the surfactant reactant and/or product possess characteristic chromophores then visible and infrared spectrometry have provided information concerning the extent of reaction or the nature of the final products. In general, spectroscopic studies alone are not likely to provide either a unique identification or a measure of the absolute amount of material taking part in a chemical reaction. This is especially true when the reactants and products are structurally similar.

This report will demonstrate the use of a multicompartment monolayer trough designed to allow a series of chemical reactions to be performed upon a well-defined monolayer and the application of high-performance liquid chromatography (LC) and vapor-phase chromatography (VPC) to separate and quantitate the resulting products. These techniques will be used to compare the hydrolysis kinetics of the surfactant diester derivative of ruthenium(II) tris(bipyridyl), I, to that of the water-soluble analogue, II.



I, R = R = $C_{18}H_{37}$
II, R = R = C_2H_5

IV, R = $C_{18}H_{37}$
V, R = C_2H_5

III

Experimental Section

Materials. The synthesis and characterization of compounds I-IV have been described[9] with the exception of V whose structure was assumed on the similarity of its absorption spectrum to IV and its intermediacy in the hydrolysis of II to III. The specific preparation of IV used for this report was synthesized as the perchlorate salt and contained 5 mol % I and 9 mol % *n*-octadecanol by LC analysis. *n*-Octadecanol (Sigma, containing 1.3 mol % *n*-hexadecanol and 0.9 mol % *n*-eicosanol), all organic solvents (Burdick and Jackson), and all inorganic compounds (reagent grade) were used as obtained. Triply distilled water was used in the preparation of the monolayer subphase solutions.

Multicompartment Monolayer Trough Design. The monolayer trough shown in Figure 1 has been fabricated from clear, acrylic plastic sheet by solvent welding trough side walls (1.91 cm wide, 0.48 cm high) onto a single piece base (244 cm × 61 cm × 1.91 cm; Ain Plastics, Inc., Mount Vernon, N.Y.) supported on a stone table top of similar dimensions. The top and inner surfaces of the side walls are made hydrophobic by rubbing with paraffin (mp 60-63 °C). When the trough is filled with distilled water to give a convex meniscus, the continuous surface area is 11 900 cm^2 (233.7 cm × 50.9 cm) and the depth is ca. 0.55 cm. The subphase volume is divided into five unequal compartments by four glass subsurface walls (1.26 cm wide × 0.45 cm high) which extend the inner width of the trough and are fixed in

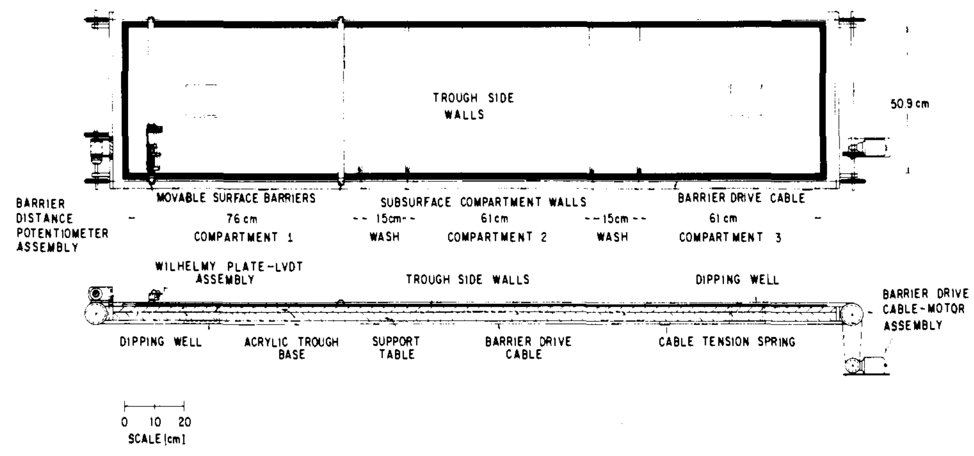


Figure 1. Multicompartment monolayer trough.

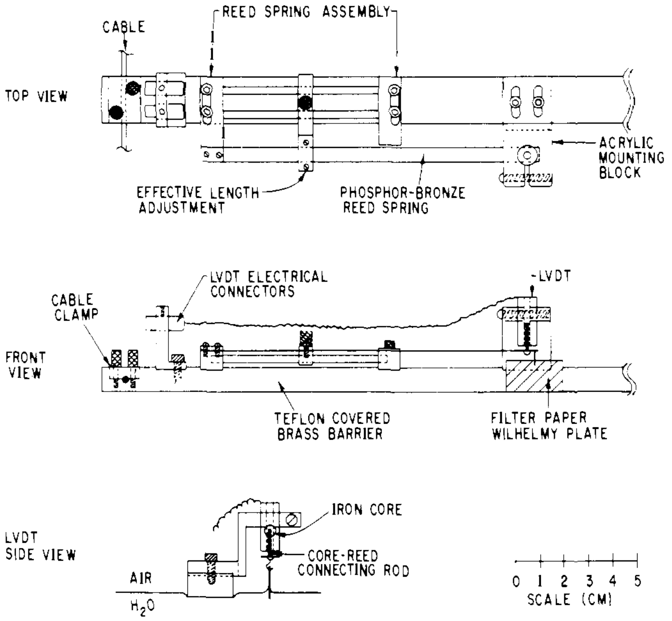


Figure 2. Detail of LVDT—Wilhelmy plate assembly.

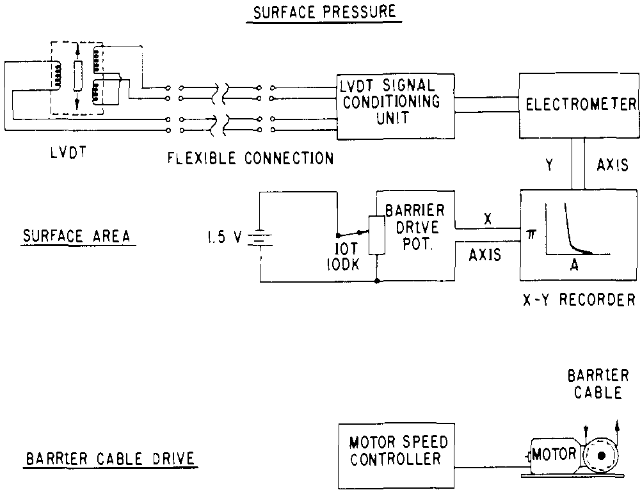


Figure 3. Schematic of electrical system for surface pressure, surface area, and barrier drive cable functions.

position with paraffin. While a thin film of water, ca 0.10 cm deep, covers the hydrophilic top surface of the submerged dividing walls, the subphase solutions within each compartment may be filled and emptied independently. In normal use, a removable hydrophilic glass strip (50.9 cm × 1.26 cm high × 0.45 cm wide) is positioned vertically on top of the subsurface barrier to minimize any intercompartment subphase diffusion. While not used in the present report, the trough is equipped with a dipping well (10.2 cm × 10.2 cm × 5.1 cm deep) at each end to allow for transfer of the monolayer off the surface onto a solid support, e.g., glass slides.

Surfactant films were constrained between the hydrophobic long sides of the trough and two movable surface barriers, defined as the "LVDT barrier" and the "compression barrier" [27.7 cm × 1.91 cm wide × 0.95 cm high, brass covered with Teflon (Temp-R-Tape Type TH, The Connecticut Hard Rubber Company, New Haven, Conn.)]. These barriers may be driven independently or together by securing them via cable clamps (see Figure 2) to two continuous loops of plastic jacketed aircraft cable (0.159 cm O.D., No. AB046-N-7-7; W. M. Berg, Inc., East Rockaway, L. I., N.Y.) running along each long side of the trough between pulleys (7.11 cm diameter) mounted on axles (0.95 cm diameter hardened stainless steel) at the ends. The cables are driven by an electric motor (Model 548, Type NSH 12R, 1/50 hp; Bodine Electric Company, New York, N.Y.) coupled to one end axle via a timing belt (0.0816 in. pitch, 0.313 in. wide) and pulleys (40 DP; motor, 5.0 cm diameter; cable axle, 7.10 cm diameter). The range of linear barrier travel speeds afforded by the motor's variable speed controller (Model 901, Bodine Electric Co.) is 0.75 to ca. 100 cm/min. The position of the cable clamped barrier(s) is determined by a precision tenturn potentiometer (100 KΩ, Helipot) coupled to second end axle via a timing belt (0.0816 in. pitch, 0.313 in. wide) and pulleys (40 DP; potentiometer, 0.95 cm diameter; cable axle, 7.95 cm diameter) which can be disengaged when not required.

As shown in detail (Figure 2), one of the movable barriers (the "LVDT barrier") carries a Wilhelmy balance to monitor surface pressure. The design is similar to that previously described by Kuhn[10] and Fromherz.[11] A phosphor-bronze metal strip (14.0 cm × 0.60 cm × 0.0381 cm) is fixed at one end and the effective length can be varied by moving a second clamping bracket (effective length used herein is 9.0 cm). The free end of the strip has a hook on its underside to suspend the Wilhelmy plate and an iron core (0.16 cm diameter × 0.30 cm length) soldered to the top of a brass screw (0-80) attached to its upper side. The core/screw moves vertically inside a linear variable differential transformer (LVDT Type 050 MHR; Schaevitz Engineering, Camden, N.J.) mounted onto the barrier with an acrylic holder. A piece of filter paper [1.2 cm (vertical) × 2.3 cm (horizontal); Schleicher and Schüll, No. 589 Black], just barely dipped (ca. 0.2 cm) into the subphase, is used as the hydrophilic plate.[10,12]

As shown in Figure 3, the LVDT is connected to an AC excitation source and detector module (Signal Conditioning Unit Model CAS-025R, Schaevitz Engineering) via two two-wire cables which can be disconnected from the barrier when not required. The DC output is fed to an electrometer (Keithley 610B) and plotted on the Y axis of an X-Y recorder (Hewlett Packard Model 2FAM). When measuring surface pressure-molecular area (Π-A) isotherms, the voltage from the barrier position sensing potentiometer-battery combination (see Figure 3) is recorded on the X axis.

The trough and barrier drive assembly are protected by four acrylic sheet covers (not shown in the figures) which slide along on Teflon glides and provide support, with access to the surface, for a variety of accessories. The trough and its covers are not thermostated but are in a room where the ambient temperature (22 ± 1 °C) is maintained by an air conditioner. Prior to attempting any monolayer work, the trough was filled with distilled water which was exchanged daily for a 2-week period in an attempt to remove any readily soluble contaminants in the plastic.

LVDT Wilhelmy Balance Calibration. The surface pressure calibration of the barrier mounted LVDT Wilhelmy balance combination was done by measuring the Π–A isotherm of *n*-octadecanol on 10^{-3} M NaCl at 22 °C and comparing it directly to that obtained under identical conditions with a conventional quartz spiral Wilhelmy balance ($\Pi/\Delta h$ = 21.7 dyn/cm/cm). In both cases, the filter paper plate was totally immersed in the subphase and allowed to drain to a constant weight while partially submerged and the resulting clean surface reference position was noted. The film area was varied by moving the "compression barrier" while keeping the "LVDT barrier" fixed. Using the quartz spiral, the surface pressure at which the change of slope occurs for octadecanol was found to be 13.8 dyn/cm (lit.[13] ~13.5 dyn/cm). By referencing the LVDT balance generated surface pressure scale to this value an overall Π–A isotherm of octadecanol identical to that using the quartz spiral was obtained. The molecular areas of the lower and upper branches of the Π–A curve extrapolated to Π = 0 are 21.5 ± 0.2 Å^2 and 20.1 ± 0.1 Å^2, respectively. After obtaining a reference reading for a clean surface, day-to-day calibration of the recorded Π scale was done by adding standard weights to the hook suspending the partially immersed paper plate (Π, weight): 35.7 dyn/cm, 0.1628 g, and 15.4 dyn/cm, 0.0714 g.

Hydrolysis Procedure Using the Multicompartment Trough. Solutions of 1.0×10^{-3} M NaCl are added to compartment 1 and both of the wash compartments. Aqueous $NaHCO_3$/NaCl (both 1.0×10^{-3} M, pH 8.2) and $HClO_4$ (1.0×10^{-2} M) are added to compartments 2 and 3, respectively. The surface of the subphase in compartment 1 is cleaned by repetitive compression barrier sweepings and contamination removed by aspiration before obtaining the reference surface pressure reading (Π = 0). With the two barriers separated by 70 cm (LVDT barrier immobile, the compression barrier clamped to cable), 75 μL of a solution of I in $CHCl_3$ (3.96×10^{-3} M, synthesized as the dichloride salt[14]) is applied dropwise to the top of a hydrophilic, rounded glass rod (0.4 cm diameter) immersed in the subphase which extends ca. 1 cm above the surface. After the addition is complete (ca. 1 min), 50 μL of pure $CHCl_3$ are used to rinse the glass rod before the latter is removed from the subphase. When ca. 3 min had elapsed from the start of the addition, the film was compressed (112 cm^2/min) to either Π = 10 or 33.3 dyn/cm. The LVDT barrier was then clamped to the cable and the film moved (59 cm/min) at constant area across the first wash compartment onto the $NaHCO_3$/NaCl subphase. The reaction time starts when the front edge of the film crosses onto the alkaline solution. The LVDT barrier was then released from the cable and the compression barrier driven (human servo control) to keep Π constant. After a time interval, the LVDT barrier was once again clamped to the cable, the film transported (59 cm/min) at constant area across the second wash compartment onto the $HClO_4$ subphase, and the LVDT barrier released from the cable in order to maintain constant Π by driving the compression barrier. When the area became constant (usually within five min), both barriers were moved apart to ca. 58-cm separation (still on compartment 3, Π observed to fall to zero) and the "skim" surface barrier (27.7 cm × 0.95 cm × 0.95 cm; Teflon coated brass) placed on the surface directly in front of the LVDT barrier (~2 cm distance). Subphase solution was carefully removed (without disturbing the monolayer film) to lower its surface to the same level as the top of the trough side walls. The clamped compression barrier was then used to compress and collapse the film against the skim barrier until ca. 0.5 cm separation distance remained. After the two barriers were carefully arranged into an elongated "V", the "skim" spatula (stainless steel, 1.0 cm wide) was immersed into the subphase at the open end of that "V" at the trough side wall sandwiched tightly between the two barriers. Thus, it can skim off the surface film while being drawn toward the closed end of the "V". The skimmed film was then dissolved in ca. 2 mL of $CHCl_3$. The area between the barriers was skimmed once again and the skim dissolved in the same $CHCl_3$ solution. A cotton tipped stick was then used to perform a final skim between the tightly closed barriers. If a colored residue was visible on the swab, it was washed off into the original $CHCl_3$ solution with a small volume (<1 mL) of fresh $CHCl_3$. The few drops of supernatant aqueous subphase which was carried along into the vial were carefully removed with a syringe and the $CHCl_3$ solution was evaporated to dryness using a N_2 stream at 45 °C. The residue was dissolved in 50% aqueous THF (0.015 M $MeSO_3H$, 0.5% HOAc) just prior to analysis by HPLC.

The monolayer hydrolysis of IV was done in the same manner having waited 15 min after applying 480 μL of a 1.0 mg/mL solution in $CHCl_3$ to the surface of 1.0×10^{-3} M NaCl in compartment 1.

Bulk Aqueous Solution Hydrolysis. The appropriate volume of a 1.06×10^{-3} M solution of II[15] in aqueous NaCl (10^{-3} M) to achieve a concentration of 1×10^{-5} to 5×10^{-7} M was transferred to a 50-mL volumetric flask, diluted to the mark with aqueous $NaHCO_3$/NaCl (both 1.0×10^{-3} M, pH 8.2), mixed, and maintained in the dark at 22 ± 1°C with agitation prior to every 150-μL aliquot removed for LC analysis. The hydrolysis was stopped upon injection into the acidic chromatography mobile phase.[16]

Chromatographic Analyses. High-performance liquid chromatographic (LC) of I–V utilized a Waters Associates Model 244 liquid chromatograph, μBondapak/C_{18} column (30 cm × 0.39 cm I.D.), and an aqueous tetrahydrofuran (THF) solvent system with added alkyl sulfonate anions according to procedures previously described.[16] *n*-Octadecanol was detected by both LC (μBondapak/C_{18}, isocratic 25% aqueous THF with *no* added alkyl sulfonates, 2.0 mL/min, ΔRI detector, retention time = 2.0 min, minimum amount detectable = 1.5×10^{-9} mol) and vapor phase chromatography (VPC). The VPC analysis employed a Varian Model 1740 gas chromatograph (183 cm × 0.2 cm I.D. OV-101 on 100/120 Var Aport 30 glass column, 200 °C, 20 psi He, FID, retention time = 26.0 min, minimum amount detectable = 1×10^{-11} mol).

Results

Trough Operations. Film Transfers. With 1.0×10^{-3} M NaCl in all compartments a film of I was formed on the surface of compartment 1 and compressed to Π = 10.0 dyn/cm. After the film is shifted (59 cm/min) at constant area across compartment 2 onto compartment 3, the surface pressure is observed to decrease by 0.5 dyn/cm. Upon return to compartment 1 an additional decrease of ca. 0.3 dyn/cm has occurred. Variations of ±0.5 dyn/cm, which are apparently due to slight distortion of the trough dimensions, are also observed as the LVDT barrier is moved along the length of the trough (stopped for measurement of Π) in the absence of a surface film.

With 1.0×10^{-3} M NaCl in compartments 1 and 2 and the intervening wash compartment, a film of *n*-octadecanol was formed on compartment 1 and compressed to Π = 10 dyn/cm leaving a film-free surface area between the first subphase wall and the compression barrier (ca. 30 cm separation). With the vertical barrier in place on top of this first subphase wall, a concentrated, deep-red solution of methyl orange in distilled H_2O was carefully pipetted into the subphase of compartment 1 forming a band ca. 3–4 cm wide across the entire width of the trough adjacent to the subphase wall. The vertical barrier was slowly removed allowing a continuous water surface to connect compartments 1 and 2. After standing ca. 5 min, it was clear that the dye was diffusing down the length of compartment 1 but was not diffusing sufficiently rapidly (if at all) across the subsurface wall to be observed visually in the wash compartment (a length of white paper had been placed between the transparent trough base and the supporting table for this experiment). The film of octadecanol was moved (59 cm/min) at constant area from compartment 1 to compartment 2. While there was no apparent dye diffusion into this latter compartment, a yellow coloration of decreasing intensity (going toward 2) was observed in the wash compartment. After several film transfers back and forth between 1 and 2, dye is observed in 2. Hence, there is little or no subphase mixing between the major compartments accompanying a single, one-way transfer of a surface film by this qualitative observation.

Trough Operations. Π–A Isotherms. A film of I (3.05×10^{-7} mol) was formed on 1.0×10^{-3} M NaCl in compartment 1 and its Π–A isotherm was measured. This Π–A curve is shown (Figure 4) in comparison to that obtained with a calibrated quartz spiral Wilhelmy balance. The surface pressure was then reduced to ca. 2 dyn/cm and the film moved at fixed area

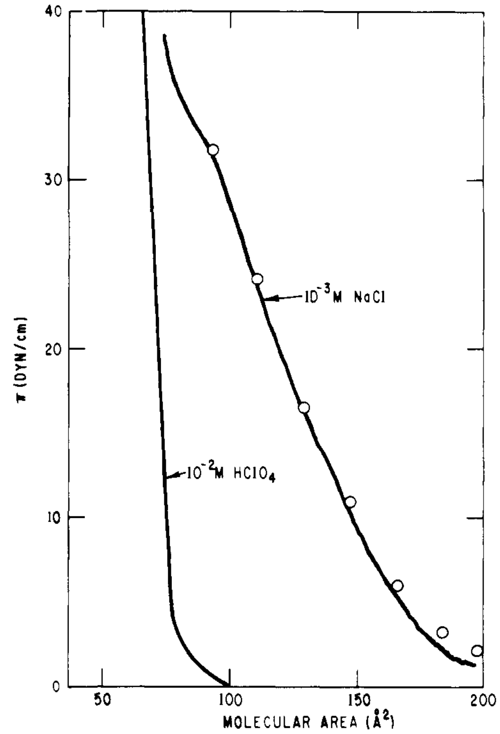


Figure 4. LVDT—Wilhelmy balance measured Π-A isotherms (22 °C) of I on 1.0 × 10^{-3} M NaCl in compartment 1 and after being shifted onto 1.0 × 10^{-2} M $HClO_4$ in compartment 3 (compression rate in both cases 108 cm^2/min), solid lines. Data obtained using quartz spiral Wilhelmy balance for I on 10^{-3} M NaCl, ⊙.

Table I. Hydrolysis of I in Monolayers, Π = 10 dyn/cm[a]

time, min	I mol × 10^9	I rel mol %	IV mol × 10^9	IV rel mol %	[III] = 100 −{[I] + [IV]} rel mol %
0	228 ± 15	100[b]	0	0	
3.5	213	93	20	9	
5.0	196	86	47	20	
7.0	186	81	52	23	
10.0	161	71	65	29	
12.5	133	58	84	37	5
15.5	102	45	91	40	15
22.5	78	34	100	44	22
30.5	45	20	118	52	28
37.6	35	15	115	51	34
37.6	32	14	121	53	33
44.8	19	8	103	45	47
60.8	17	8	101	44	48
75.2	10	5	72	32	63
90.3	10	5	82	36	59
120.5	6	3	42	18	79
150.5	6	3	47	21	76
228	5	2	38	17	81

[a] Monolayer Π = 10.0 ± 0.5 dyn/cm, 1.0 × 10^{-3} M aqueous $NaHCO_3$/NaCl, pH 8.2, 22–23 °C. [b] Absolute recovery of I at t = 0 is 78 ± 5 mol % (average of seven experiments); 292 × 10^{-9} mol of I originally applied to surface.

across 10^{-3} M NaCl in compartment 2 onto 10^{-2} M $HClO_4$ in compartment 3. After standing 5 min, a second Π-A curve, also shown in Figure 4, was recorded.

Trough Operations. Hydrolysis of I at Constant Π. Films of I (3.05 × 10^{-7} mol) were formed on 1.0 × 10^{-3} M NaCl in compartment 1, compressed to Π = 10 dyn/cm, and moved across the wash surface onto various alkaline solutions (1.0 × 10^{-3} M $NaHCO_3$/NaCl, pH 8.2; 1.0 × 10^{-3} M borate/KCl, pH 9.0; 1.0 × 10^{-2} M borate/KCl, pH 10.0) contained in compartment 2. Keeping Π constant (10.0 ± 0.5 dyn/cm), the film shrinkage relative to the original area observed on 10^{-3} M NaCl was monitored as a function of time (Figure 5). After an initial rapid decrease, the shrinkage slowly approaches the area expected for a completely hydrolyzed film (two octadecanol molecules per molecule of I). In one long-term experiment utilizing 1.0 × 10^{-3} M $NaHCO_3$/NaCl, aliquots (10 mL) of this subphase were withdrawn periodically from under the film up to a hydrolysis time of 150 min and shown to have a pH (8.1 ± 0.1) invariant with time.

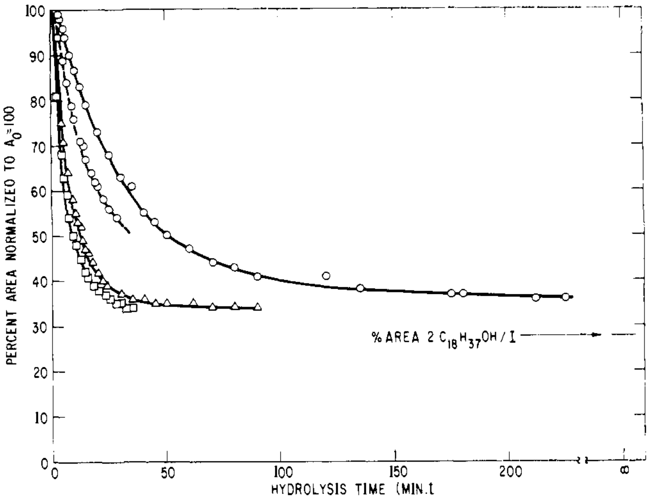


Figure 5. Plot of percent area vs. hydrolysis time for I as a function of pH at constant surface pressure (22–3 °C). All percentages expressed relative to original area (A_0 = 100%) observed for I on 1.0 × 10^{-3} M NaCl in compartment 1. Key: -⊖-, 1.0 × 10^{-3} M $NaHCO_3$/NaCl, pH 8.2, 10 dyn/cm; △, 1.0 × 10^{-3} M borate/KCl, pH 9.0, 10 dyn/cm; ⊡, 1.0 × 10^{-2} M borate/KCl, pH 10.0; --⊖—, 1.0 × 10^{-3} M $NaHCO_3$/NaCl, pH 8.2, 33.3 dyn/cm.

Trough Operations. Recovery of Films for Chromatographic Analysis. Films of I (3.05 × 10^{-7} mol) were formed on 1.0 × 10^{-3} M NaCl in compartment 1, compressed to Π = 10 dyn/cm, and transferred at fixed area across 10^{-3} M NaCl containing subphases onto 1.0 × 10^{-2} M $HClO_4$ in compartment 3. After moving the barriers to their maximum separation (ca. 58 cm; Π = 0 at barrier separations ≥35 cm), the "skim barrier" was placed ca. 2 cm in front of the LVDT barrier such that the Wilhelmy balance assembly would not obstruct film recovery. It has been demonstrated by sprinkling talc onto the surface that the film (at Π = 0 dyn/cm) remains stationary while moving the LVDT barrier back ca. 10 cm. Hence, no film is trapped between the LVDT and skim barriers. The film is compressed and collapsed into visibly reddished threads between the skim and compression barriers. The film is then skimmed off and analyzed quantitatively by LC. The average absolute recovery of I observed for seven separate trials was 78 ± 5 mol % with no hydrolysis product (IV) present.

Films of *n*-octadecanol (6.00 × 10^{-7} mol) manipulated in the same fashion showed absolute recoverys of 80, 96 (two experiments only), and 90 ± 3 mol % as analyzed by LC and VPC, respectively. The recovery efficiency of an *n*-octadecanol film spread, collapsed, and recovered from 10^{-2} M $HClO_4$ was the same (90 mol %) as that observed for films transferred from other compartments.

Hydrolysis of I in Monolayer Films. Stable films of I could be formed on 10^{-3} M NaCl and hydrolyzed according to the procedure given in the Experimental Section. The results are given in Tables I and II and plotted for Π = 10 dyn/cm in Figure 6. The kinetic rate constants are summarized in Table IV.

Under the LC conditions used for analysis of the surfactant ruthenium compounds, III elutes at the column void volume

Table II. Hydrolysis of I in Monolayers, Π = 33.3 dyn/cm[a]

time, min	I mol × 10^9	I rel mol %	IV mol × 10^9	IV rel mol %
0.0	234	100[b]	0	0
3.2	210	90	11	5
5.2	161	69	29	12
7.1	142	60	33	14
10.2	155	66	18	7
15.2	105	45	24	10
20.0	93	40	32	14
30.2	57	24	23	10

[a] Monolayer: Π = 33.3 ± 0.5 dyn/cm, 1.0 × 10^{-3} M $NaHCO_3$/NaCl, pH 8.2, 22-23 °C. [b] Absolute recovery of I at t = 0 is 77 mol %, 305 × 10^{-9} mol of I originally applied to surface.

Table III. Hydrolysis of IV in Monolayers[a]

time, min	IV mol × 10^9	IV rel mol %
0	161 ± 7	100[b]
39.4	104	65
61	89	55
90	64	39
165	27	17

[a] Monolayer: Π = 10.0 ± 0.5 dyn/cm, 1.0 × 10^{-3} M $NaHCO_3$/NaCl, pH 8.2, 21-22 °C. [b] Absolute recovery of IV at t = 0 is 51 mol %.

with other components (THF oxidation products) and cannot be routinely measured. In the expectation that this water-soluble product would diffuse away from the surface film during the course of the reaction, the entire bicarbonate and wash (separating compartments 2 and 3) subphase volume (ca. 2.5 L) was recovered from two of the experiments, concentrated to dryness with the rotary evaporator, and analyzed by LC using conditions[16] for water-soluble ruthenium derivatives. The absolute recoveries of III for hydrolysis times of 75.2 and 150.5 min are 37 and 31 mol %, respectively. No control experiment was done to determine how much III was lost during the recovery, concentration, and other experimental manipulations.

Due to the lack of precision in analyzing for *n*-octadecanol in the presence of ruthenium compounds by LC (differential refractive index detector) at this sample level and the apparent thermal degradation of I to *n*-octadecanol in the hot injection port of the gas chromatograph, VPC analysis for the octadecanol was done only after a single long-term hydrolysis to confirm its presence as the major product. A film of I was formed on 10^{-3} M NaCl, hydrolyzed on 10^{-3} M $NaHCO_3$/NaCl and then on ca. 10^{-2} M NaOH until no further area shrinkage was noted, and recovered from 10^{-2} M $HClO_4$. The *n*-octadecanol reaction yield was found to be 59 mol %.

Hydrolysis and Stability of IV in Monolayer Films. A film of IV (3.1 × 10^{-7} mol) formed on 10^{-2} M $HClO_4$ and compressed to Π = 10 dyn/cm did not exhibit any decrease in area with time (30 min) and gave an absolute recovery for IV of 90 mol %. In contrast, a second film, identical in composition, showed a slow shrinkage at Π = 10 dyn/cm on 10^{-3} M NaCl over 30 min (the least-squares determined first-order rate constant for shrinkage is 3.6 × 10^{-3} min^{-1}, r^2 = 0.98) and gave a 43 mol % recovery of IV after shifting the film onto aqueous $HClO_4$. Upon compression to Π = 33.3 dyn/cm on 10^{-3} M NaCl, a third film showed an even faster rate of shrinkage (estimated first-order rate constant ≥2 min^{-1}) and allowed only a 4 mol % absolute recovery after 30 min (as usual the film was shifted to aqueous $HClO_4$ for skimming).

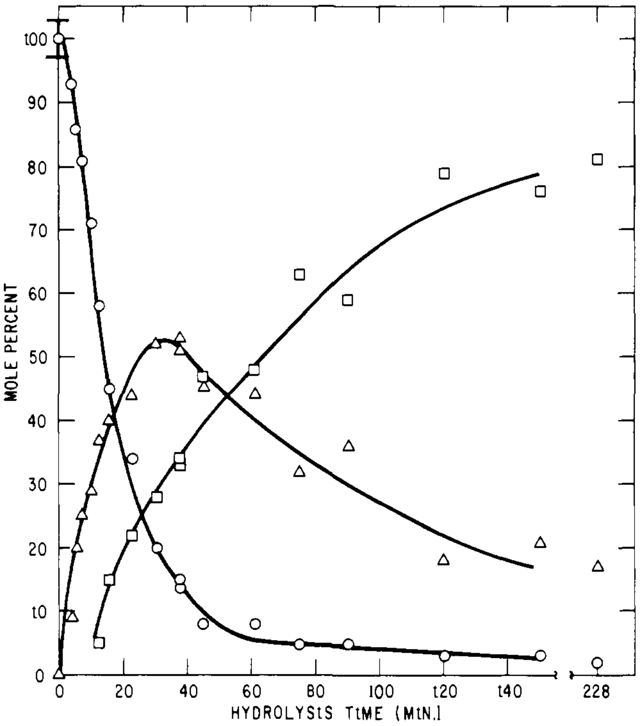


Figure 6. Relative concentrations of reactant (I, ○) and products (IV, △; III, ⊡) during hydrolysis on 1.0 × 10^{-3} M $NaHCO_3$/NaCl (10.0 ± 0.5 dyn/cm, 22-23 °C, initial amount of I is 3.0 × 10^{-7} mol at a surface concentration of 6.7 × 10^{13} molecules/cm^2) as determined by LC. The amounts of III were calculated from 100 − {[I] + [IV]}.

Table IV. Kinetic Summary: Hydrolysis of I and IV in Monolayers

reaction description [compd, Π (dyn/cm), reaction time (min)]	$k_{-\mathrm{I}}(r^2)$[a] × 10^2 min^{-1}	$k_{-\mathrm{IV}}(r^2)$[a] × 10^2 min^{-1}
I, Π = 10, 0-45, hydrolysis[b,c]	5.3 (0.99)	
I, Π = 10, 45-150, hydrolysis[b,c]	1.1 (0.89)	0.90 (0.76)
I, Π = 33.3, 0-30, hydrolysis[b]	4.6 (0.97)	
IV, Π = 10, 0-165, hydrolysis[b]		1.1 (1.00)
IV, Π = 10, 0-30, dissolution[d]		0.40 (0.95)
IV, Π = 33.3, 0-30, dissolution[d]		≳200
IV, Π = 10, 0-30, dissolution[e]		0

[a] Pseudo-first-order rate constants derived for the disappearance of I and IV by fitting the LC concentration (hydrolysis) or surface area (dissolution) data to an exponential curve by a least-squares linear regression; r^2 is the coefficient of determination. [b] Subphase: 1.0 × 10^{-3} M $NaHCO_3$/NaCl, pH 8.2, 22-23 °C. [c] The plot of log [I] vs. time shows an intersection point at t = 45 min. [d] Subphase: 1.0 × 10^{-3} M NaCl, 22 °C. [e] Subphase: 1.0 × 10^{-2} M $HClO_4$, 22 °C.

The results for the hydrolysis of IV on 10^{-3} M $NaHCO_3$/NaCl are shown in Table III and the derived kinetic rate constants summarized in Table IV.

Hydrolysis of II in Homogeneous Aqueous Solution. The hydrolysis of II (1.0 × 10^{-4} M) in aqueous alkaline solution (1.0 × 10^{-2} M borate/KCl, pH 10.0, 20 ± 1 °C) to V and then to III is shown in Figure 7.[16] The time dependence of the reaction composition can be calculated for consecutive pseudo-first-order reactions with k_1 = 8.62 × 10^{-2} min^{-1} and k_2 = 2.6 × 10^{-2} min^{-1}. The close fit of theory with the experimental points is evident from Figure 7. The hydrolyses of several concentrations of II (1.0 × 10^{-5} M, 1.0 × 10^{-6} M, 5.0 × 10^{-7} M) in 1.0 × 10^{-3} M $NaHCO_3$/NaCl (pH 8.1 ± 0.1) follow similar kinetics at a slower rate as shown in Table V.

Discussion

Chromatography and Reactions in Monolayer Films. It had been previously observed that the area of a monolayer of I

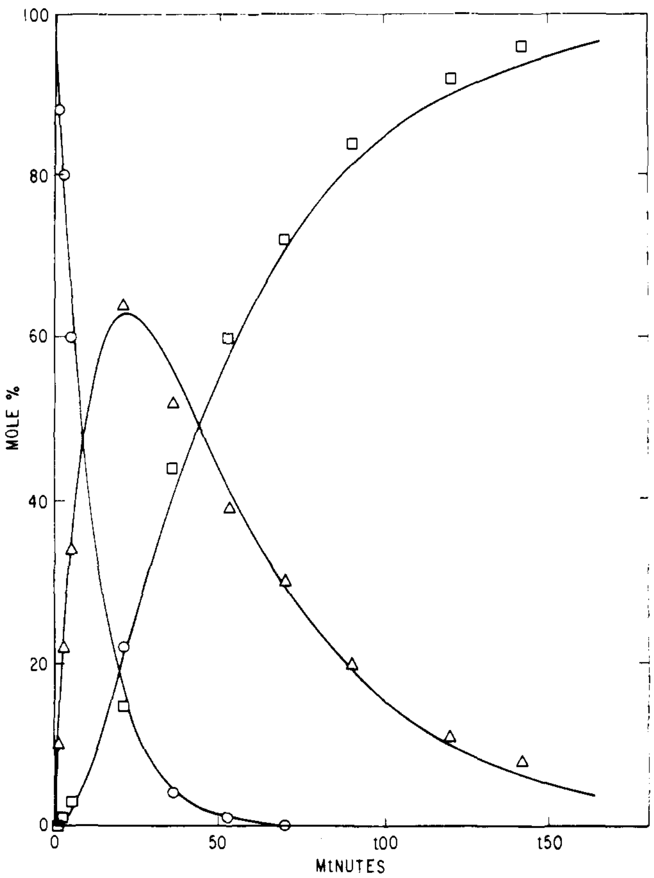
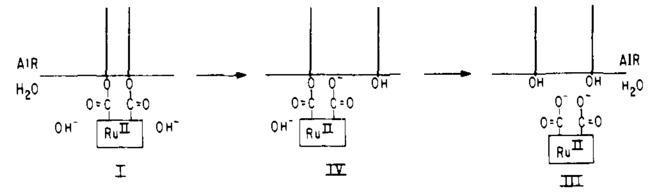


Figure 7. Relative concentrations of reactant (II, ○) and products (V, △; III, □) during hydrolysis in aqueous 1.0×10^{-2} M borate/KCl buffer (pH 10.0, 20 ± 1 °C, initial [II] = 1.0×10^{-4} M) as determined by LC. The absolute mass balance at each sampling is 101 ± 2 mol %. The lines shown are calculated for consecutive, pseudo-first-order reactions, with $k_1 = 8.62 \times 10^{-2}$ min^{-1} and $k_2 = 2.16 \times 10^{-2}$ min^{-1}.

spread on alkaline subphase and held at constant surface pressure decreases with time whereas that of a monolayer spread on a subphase of pH < 7 did not.[9] By analogy to the chemistry observed for I in alkaline 50% aqueous THF and II in alkaline aqueous solution,[16] it was expected that the diester surfactant was hydrolyzing to the water-soluble dicarboxylate, III, and *n*-octadecanol via IV.



Assuming the ester hydrolysis to be only a function of the observed film shrinkage, the rate of this hydrolysis was observed to increase with increasing pH and surface pressure in a similar fashion to the data of this study plotted in Figure 5. However, a quantitative analysis of the progress of the hydrolysis of I based on these data is complicated by the known extreme sensitivity of the Π-A isotherms of these monolayers to anions contained in the subphase, the substantial deviations from additivity occurring in mixed films, the irreproducible behavior of films of pure IV when compressed on neutral chloride containing or alkaline subphases, the decreasing surface charge density as the reaction proceeds, and the expected diffusion of the water-soluble III away from the surface.[9] It was for these reasons that the quantitation of I and IV by the LC techniques used successfully to analyze monolayers desorbed from glass slides in the previous study[9] was applied to monolayer films recovered directly from the air-water interface in the present report. While it has been long felt desirable to obtain a quantitative measure of the composition of reactions occurring in monomolecular films,[8] only in three instances have the unique properties of a chromatographic based analytical technique to separate multicomponent mixtures been utilized. Shah and Schulman used thin-layer chromatography (TLC) to present qualitative but direct evidence that snake venom contained in the subphase hydrolyzes lecithin monolayers into lysolecithin and free fatty acid.[17] Charbonneau and Kowkabany described the combined use of the TLC and a ^{14}C-radio assay method to provide a description of the alkaline hydrolysis of tripalmitin.[25] More recently, Naegele and Ringsdorf showed by TLC that the product mixture resulting from the UV photopolymerization of octadecyl methacrylate monolayers contained "much" unreacted monomer.[3] It is now clear that the use of LC and VPC to detect and quantitate the small amounts of material contained in surface films should be considered standard tools whenever chemical reactions in monolayers are studied.

Table V. Kinetic Summary: Hydrolysis of II in Aqueous Solution

	II → V		V → III	
$[\mathrm{II}]_0$, mol/L[a]	k_1, min^{-1} [d]	r^2 [d]	k_2, min^{-1} [e]	k_1/k_2
1.0×10^{-4} [b]	8.6×10^{-2}	0.99	2.2×10^{-2}	3.9
1.0×10^{-5} [c]	4.9×10^{-3}	1.00	1.0×10^{-3}	4.9
1.0×10^{-6} [c]	5.2×10^{-3}	0.99	2.0×10^{-3}	2.6
5.0×10^{-7} [c]	5.0×10^{-3}	0.97	~7×10^{-4}	~7

[a] Reaction temperature = 21-22 °C. [b] 1.0×10^{-2} M borate/KCl, pH 10.0. [c] 1.0×10^{-3} M $NaHCO_3$/NaCl, pH 8.2. [d] Data were fit to an exponential curve $[\mathrm{II}] = [\mathrm{II}]_0 e^{-k_1 t}$ by a least-squares linear regression; r^2 is the coefficient of determination. [e] k_2 was obtained by a trial and error fitting of the concentration data of V and the calculated k_1 to the consecutive, pseudo-first-order reaction equation: $[\mathrm{V}] = [\mathrm{II}]_0 [k_1/(k_2 - k_1)] [e^{-k_1 t} - e^{-k_2 t}]$.

Multicompartment Troughs and Reactions in Monolayer Films. The mechanics of performing the hydrolytic reaction of I in monolayer films requires several operations: (1) the film must be spread at the interface and compressed to the desired surface pressure; (2) the hydrolysis reaction should occur under conditions where the surface pressure is held constant and can be quenched quickly; and (3) the film must be recovered as quantitatively from the interface as possible. It became evident that these steps might best be accomplished in a multicompartment trough such as the one described herein. Troughs employing multiple subphase compartments have been used previously by Langmuir and Waugh to study pressure-soluble components of protein monolayer films[18] and more recently in elegant studies by Fromherz of the adsorption of water-soluble proteins onto lipid monolayers.[11,19]

Figure 8 shows a schematic representation of the trough operations involved in the hydrolysis of I. The initial step involves the formation of a well-defined monolayer film on a nonhydrolyzing subphase. Hence, any instability in the film such as might occur if the surfactant were slightly water soluble or underwent counterion exchange with the bulk subphase can be detected and distinguished from any changes accompanying the hydrolysis reaction itself. Furthermore, the film can be compressed to the desired surface pressure prior to bringing it into contact with alkaline subphase thus eliminating that interval of time (ca. 5 min) on single-compartment troughs starting when the initial drop of spreading solution touches the interface and continuing through solvent evaporation until the desired surface pressure is reached.

The film can then be laterally transported across the subsurface walls at constant area onto the alkaline subphase by simultaneously moving the two surface barriers. By driving only one of the surface barriers while using the other as a fixed platform for the surface pressure detector, the film area can be adjusted to maintain a constant Π. The hydrolysis reaction is then quenched by moving the film across the wash compartment to minimize the volume of entrained alkali onto an acid-containing subphase. Previous studies had clearly shown that the hydrolysis reaction in bulk solution is stopped immediately by acid quenching.[16] In addition to supplying protons, aqueous perchloric acid was chosen for the strong condensing effect the perchlorate anion has upon films of I (see Figure 4 for comparison of 10^{-3} M NaCl and 10^{-2} M $HClO_4$ upon the Π-A isotherm of I) and the fact that IV is known to form stable films on perchlorate-containing subphases.[9] Films of I on aqueous perchloric acid can be collapsed into visibly reddish threads while attempts to do so on aqueous hydrochloric acid leads to the subphase overflowing the side walls of the trough with resultant material loss. The collapsed, thicker film of I is easily skimmed off using a spatula sandwiched between two surface barriers and dissolved in an appropriate solvent. This solution of the reacted monolayer film has been analyzed directly by LC, VPC, or optical spectrometry as appropriate.

While this multicompartment trough has been used for performing condensation polymerization reactions in surface films[20] as well as the hydrolysis experiments described here, some degree of uncertainty remains concerning the procedures used due to the differences in absolute recovery observed for I, IV, and *n*-octadecanol in control experiments. Since both IV and *n*-octadecanol could be recovered in 90 mol % from films spread *and* collapsed on 10^{-2} M $HClO_4$ (an experiment using I was not done), this value has been assumed to be indicative of the efficiency of removing a surface film from the interface. The recovery of only 78 ± 5 mol % I in experiments involving lateral film shifts suggest some loss of material prior to film skimming (e.g., on the sides of the trough). However, the fact that 90 mol % of *n*-octadecanol was recovered after undergoing the same film shifts may indicate the need to tailor the lateral film transport speed to the nature of the surface film.

Hydrolysis Kinetics. Whereas rate constants derived for the sequential hydrolysis, II → V → III, in homogeneous solution are in quantitative agreement with simple consecutive pseudo-first-order reaction kinetics[21] (as shown in Figure 7 and summarized in Table V), the rate laws governing the monolayer hydrolyses, I → IV → III, are not so clear. The rate of alkaline hydrolysis of ester molecules in monolayers has been found to be a function of several parameters: (1) the concentration of *all* anions as well as hydroxide ion in the underlying aqueous solution, (2) the tightness of packing of molecules in the film, and (3) the surface electrical charge density.[22] Since I and IV are molecules bearing a double and single positive charge, respectively, monolayer films formed from such materials will possess a high positive charge density. In order to obtain a state of electrical neutrality in the interfacial region, a high concentration of negatively charged ions from the surface will be present adjacent to the film. This surface hydroxide concentration can be estimated from the Boltzmann expression,[22]

$$\ln\,[OH^-]_{surf} = \ln\,[OH^-]_{bulk} + \frac{e\Psi}{kT}$$

where $kT/e = 25.4$ mV and the surface electrical potential, Ψ, can be approximated using the Davies equation,

$$\Psi = \frac{2kT}{e}\sinh^{-1}\left[\frac{z134}{Ac^{1/2}}\right]$$

where z is the number of charges per surfactant molecule, A is the molecular area in Å^2, c is the molar concentration of salt in the subphase, and Ψ is expressed in mV. For a bulk pOH 5.8 (1.0×10^{-3} M $NaHCO_3$ + 1.0×10^{-3} M NaCl), films of I ($z = 2$, $A = 143$ Å^2, $c = 2 \times 10^{-3}$ M, $\Pi = 10$ dyn/cm) and IV ($z = 1$, $A = 105$ Å^2, $c = 2 \times 10^{-3}$ M, $\Pi = 10$ dyn/cm) increase the surface hydroxide concentration significantly to pOH 1.9 and 2.3, respectively. This calculation predicts that hydrolysis will proceed faster in a monolayer spread on an alkaline subphase than in a homogeneous solution of the same bulk pOH. It is also expected that the rate of ester hydrolysis should decrease as the hydrolysis of I proceeds such that $k_{-IV} < k_{-I}$ in accord with the decreasing interfacial hydroxide concentration. Following Davies we may calculate

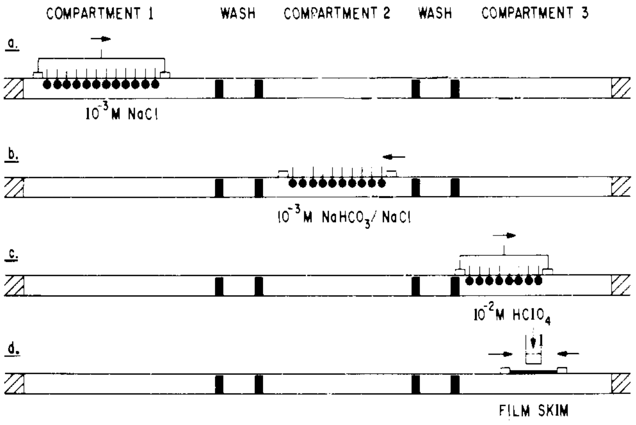


Figure 8. Schematic description of operations involved in the hydrolysis reaction of I in monolayer films at the air–water interface. Operations: (a) apply $CHCl_3$ solution of I to surface of 1.0×10^{-3} M NaCl, allow $CHCl_3$ to evaporate, and compress film to desired surface pressure; (b) shift film at constant area across 1.0×10^{-3} M NaCl in first wash compartment onto alkaline subphase and maintain constant Π by varying barrier separation; (c) shift film at constant area across 1.0×10^{-2} M $HClO_4$ to stop hydrolysis; (d) collapse film while on perchloric acid, skim off resulting thick film, and dissolve in $CHCl_3$.

$$k_{-I}/k_{-IV} = 2e^{(\Psi_{2+}-\Psi_{1+})e/kT} = 2e^{225-(205/25.4)} = 4.4$$

where the prefix 2 adjusts for I having two ester groups.

Turning to the experimental data of this report, a plot of log [I] vs. time ($\Pi = 10$ dyn/cm, 1.0×10^{-3} M $NaHCO_3$/NaCl) shows the disappearance of I as quantitatively described by two first-order rate constants, $k_{-I} = 5.3 \times 10^{-2}\ \text{min}^{-1}$ (early) and $1.1 \times 10^{-2}\ \text{min}^{-1}$ (late), whose straight lines intersect at $t \approx 45$ min. The appearance/disappearance of IV in this same reaction cannot be fitted to the simple pseudo-first-order consecutive reaction rate expression,[21]

$$[IV] = [I]\left[\frac{k_1}{k_1 + k_2}\right]\left[e^{-k_1 t} - e^{-k_2 t}\right]$$

over any interval of time. However, the disappearance of IV ($t > 40$ min) can be fitted (only fair match, $r^2 = 0.76$) to first-order kinetics, $k_{-IV}^{obsd} = 9.0 \times 10^{-3}\ \text{min}^{-1}$. A separate series of experiments starting with IV gives an almost identical first-order rate constant, $k_{-IV}^{obsd} = 1.1 \times 10^{-2}\ \text{min}^{-1}$. These observed rate constants must be corrected for the dissolution of IV into the subphase during the hydrolysis as estimated by the first-order film shrinkage (k_{-IV}^{sol}) observed on 1.0×10^{-3} M NaCl ($\Pi = 10$ dyn/cm): $k_{-IV} = k_{-IV}^{obsd} - k_{-IV}^{sol} = (1.1 - 0.4) \times 10^{-2}\ \text{min}^{-1} = 7.0 \times 10^{-3}\ \text{min}^{-1}$. LC analysis of films recovered from various subphases clearly confirms dissolution of IV from the monolayer in the case of 1.0×10^{-3} M NaCl.

Thus, a comparison of the monolayer and bulk phase hydrolyses (pOH 5.8) shows qualitative agreement with theory: $k_{-I} \approx 10k_{-II}$ and $k_{-IV} \approx 7k_{-V}$. It is clear however that the observed rate constants for the hydrolyses in monolayers are lower than expected from the calculated surface pOH.

A second comparison also shows a qualitative agreement with theory: $k_{-I}/k_{-IV} = 7.6$ (experiment) vs. 4.4 (calculated).

An alternative, but similar, comparison is suggested by the rate enhancing effect of incorporating a small amount of quaternary amine surfactant into a film of octadecyl acetate undergoing alkaline hydrolysis by Davies.[22] The disappearance of I according to *two* rate constants may reflect the higher surface charge density found in the early portion of the sequential hydrolysis reactions ($t < 20$ min) where the doubly charged I predominates than that at longer reaction times ($t > 40$ min) where I is only a minor component in the mainly singly charged film. The calculated rate ratio,

$$\frac{k_{-I}(t < 20)}{k_{-I}(t > 40)} = e^{(\Psi_{2+} - \Psi_{1+})e/kT} = 2.2$$

is lower but close to the value observed, 4.8.

Lastly, the surface change density may be increased substantially by raising the surface pressure at which I is hydrolyzed. For films of I at $\Pi = 33.3$ dyn/cm pOH is 1.6 ($z = 2$, $A = 90$ Å^2, $c = 2 \times 10^{-3}$ M) in comparison to pOH 1.9 obtained previously for $\Pi = 10$ dyn/cm. As before, the theoretical value,

$$\frac{k_{-t}(\Pi = 33.3)}{k_{-t}(\Pi = 10)} = e^{(\Psi_{30} - \Psi_{10})e/kT} = 2.5$$

and the experimentally derived ratio, 0.9, show little quantitative agreement. It is of import to note that a comparison based only on film shrinkage (Figure 5) would suggest a faster reaction proceeded at the higher surface pressure whereas quantitative analysis of the recovered films show little, if any, difference. LC analysis clearly shows that IV has a very high rate of dissolution at 33.3 dyn/cm (Table IV) and a constant, equilibrium concentration of IV in the surface film is attained very rapidly in the hydrolysis reaction starting with I (Table II).

The deviations of the experimental values from those calculated may reflect the interfacial ion concentration uncertainties caused by slow diffusion away from the surface of both III and IV, orientation changes at the interface upon going from I to IV, as well as deficiencies in the theory treating monolayer films of ionized surfactant molecules.[23] Nevertheless, the rate enhancement obtained by having a positively charged surface film rather than a neutral film is striking. In order to achieve experimentally reasonable rates for the hydrolysis of ethyl octadecanoate, Alexander and Rideal[24] were required to employ 1 N NaOH (pOH 0!) in the subphase. The hydrolysis rate constant observed, $k = 2.09 \times 10^{-2}$ min^{-1} (21.2 °C, 3 dyn/cm), lies between $k_{-\mathrm{I}}$ and $k_{-\mathrm{IV}}$ obtained in this study on a subphase having a much lower hydroxyl ion concentration, pOH 5.8. Furthermore, while a tenfold difference was noted between the rates of hydrolysis for the positively charged ester contained in the surface film and in homogeneous solution, Alexander and Rideal reported for neutral esters that the reaction velocity and activation energy were approximately the same in both environments.[26]

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(26) NOTE ADDED IN PROOF: For a recent elegant use of VPC to study a chemical reaction in monolayers adsorbed onto a Pt surface, see M. A. Richard, J. Deutch, and G. M. Whitesides, *J. Am. Chem. Soc.*, **100**, 6613 (1978).