# Effect of ionization and cation selectivity on the expansion of stearic acid monolayers

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**Abstract**  Force–area isotherms of stearic acid and stearic acid–stearyl alcohol mixtures were investigated on alkaline subphases that contained Tris, $Na^+$, or $K^+$ cations and that varied in pH and ionic strength. The monolayer behaved as though ionization was effectively complete in the expanded region of the force–area isotherm. Surface pressure in this region was independent of pH and varied inversely with ionic strength as predicted by the Davies equation. The monolayer behaved as a partially ionized film in the plateau region of the force–area isotherm. Surface pressure in this region varied directly with pH and ionic strength as predicted by a modified Davies equation for partially ionized monolayers. The neutral molecule, stearyl alcohol, exerted a large condensing effect on the ionized film at pH 12.8, and this condensing effect also supported the concept that a partially ionized stearic acid film existed in the plateau region of the force–area isotherm. A greater binding affinity for $Na^+$ than for $K^+$ showed that the stearate anion surface behaved as a strong field at pH 10 and above, and a greater binding affinity for $K^+$ than for $Na^+$ showed that the stearate anion surface behaved as a weak field at pH 9. The weak field explained in part the anomalous binding affinity of the large Tris cation for the stearate monolayer at pH 9.

**Supplementary key words**  force–area isotherm · Tris · sodium · potassium · cation binding · pH · ionic strength · strong field · weak field · stearyl alcohol · condensing effect · desorption

HIGHLY SPECIFIC cation binding sequences have been deduced from the surface properties of ionizing monolayers (1–5). These binding sequences provide another model and extend the strong-field and weak-field cation selectivity patterns established for various minerals, ion exchangers, resins, collodion membranes, and most importantly, the penetration of cations through some biological membranes (6, 7). Several recent studies have shown that one surface property, surface area at a given surface pressure, depended on the alkali metal cation and varied directly with the pH and the ionic strength of the subphase (2–5). Sears and Schulman (2), Goddard, Smith, and Kao (3), and Goddard, Kao, and Kung (4) examined fatty acid monolayers on strongly alkaline subphases where the pH of the subphase was 11.8 or greater and the ionic strength varied from 0.01 to 1.0. These investigators found a strong-field $Li^+ > Na^+ > K^+$ binding sequence for alkali metal cations. Rosano, Christodoulou, and Feinstein (5), studying fatty acid monolayers at pH 10.35 and 0.5 ionic strength, noted irregular cation binding sequences for several fatty acids. With low ionic strength subphases, Shah (8) found that the Tris cation markedly expanded the monolayer at pH 9 even though the monolayer remained condensed on glycine–sodium glycinate at pH 10. Sears and Schulman (2) found a $K^+ > Na^+$ reversal in the binding sequence with the condensed stearic acid film on 0.5 M bicarbonate subphases at pH 8.5. These studies prompted our reinvestigation of film expansion in ionizing monolayers.

## MATERIALS AND METHODS

Stearic acid (Applied Science Laboratories Inc., State College, Pa.) and stearyl alcohol (Hormel Institute, Austin, Minn.) were applied to the Langmuir trough in hexane solutions. $n$-Hexane was purified as previously described (9). The Langmuir trough and the film balance were used as previously described (9). The force–area ($\pi$-A) isotherms were generated at 15 $\mathrm{\mathring{A}}^2$/molecule/min. All film balance measurements were made at the ambient temperature, 24–26°C.

Constant pressure–variable area measurements were obtained with a floating barrier and piston oils as previously described (10). Castor oil, which generated 17–19 dynes/cm at pH 2.1 and 16.5–18.0 dynes/cm

at pH 12.8, and tri-*m*-tolyl phosphate, which remained constant at 9.5 dynes/cm on all subphases, were used as piston oils. The temperature was maintained at 25°C.

Subphase buffers at pH 8 and pH 9 and 0.05 ionic strength were prepared with Tris–HCl, glycine–sodium glycinate, and sodium bicarbonate–sodium carbonate (11). Subphases at pH 9, pH 10, and pH 10.8 were prepared with sodium bicarbonate–sodium carbonate or potassium bicarbonate–potassium carbonate buffers at 0.1 ionic strength (11). The ionic strength of these subphases was increased to approximately 1.0 by adding 0.9 M sodium or potassium chloride and readjusting the pH with concentrated sodium or potassium hydroxide. Other alkaline subphases contained 0.01 N sodium or potassium hydroxide and 0.09 M sodium or potassium chloride (pH 11.8), 0.1 N sodium or potassium hydroxide (pH 12.8), and 0.1 N sodium or potassium hydroxide and 0.9 M sodium or potassium chloride (pH 12.7). The pH of the subphases remained constant or decreased only 0.05 pH unit during surface measurements. The reference subphase for unionized stearic acid contained 0.1 M sodium chloride and 0.01 N hydrochloric acid (pH 2.1). All subphases contained 0.1 mM EDTA.

## RESULTS

### Effect of Tris on film expansion

Since Shah (8) noted film expansion with Tris–HCl at pH 9 and 0.05 ionic strength and very little film expansion with glycine–sodium glycinate at pH 10 and 0.05 ionic strength, we examined $\pi$-A isotherms at pH 9 and 0.05 ionic strength with several subphase buffers. In our studies, the anomalous film expansion of stearic acid spread on Tris–HCl at both pH 8 and pH 9 was absent when sodium bicarbonate and glycine–sodium glycinate buffers were substituted for Tris–HCl (Fig. 1). Small concentrations of Tris such as 0.01 M in 0.05 M sodium chloride adjusted to pH 9 had no effect on film expansion, and a monolayer on this subphase coincided with Na$^+$-containing buffers adjusted to pH 9 and 0.05 ionic strength.

### Effects of sodium and potassium cations and pH and ionic strength on film expansion

When stearic acid was spread on 0.1 and 1.0 ionic strength subphases which varied from pH 10 to pH 11.8, the surface pressure of the phase transformation varied directly with the pH and ionic strength (Fig. 2). These observations confirmed studies by Goddard et al. (3, 4) and Rosano et al. (5). At pH 12.7–12.8, a phase transformation which was largely unaffected by ionic strength occurred on Na$^+$-containing subphases (Fig. 2).
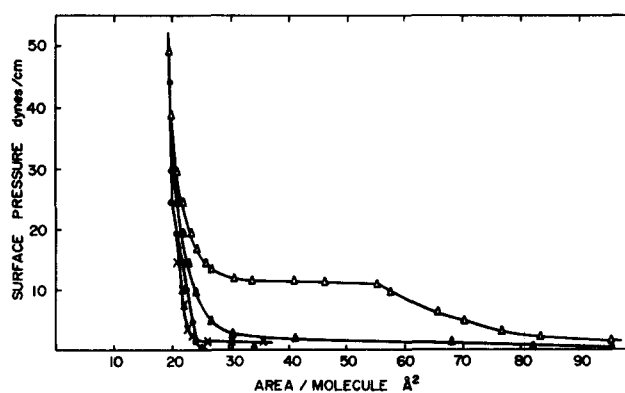


FIG. 1. $\pi$-A isotherms for stearic acid spread on 0.05 ionic strength subphases. X, sodium bicarbonate–sodium carbonate and glycine–sodium glycinate, pH 9; △, Tris–HCl, pH 9; ▲, Tris–HCl, pH 8; O, unionized stearic acid, pH 2.1 (0.01 N hydrochloric acid and 0.1 M sodium chloride). Data represent mean values from seven isotherms.

A phase transformation occurred on a K$^+$-containing subphase at pH 12.8 and 0.1 ionic strength but not at pH 12.7 and 1.0 ionic strength (Fig. 2). Rosano et al. (5) found a phase transformation on a K$^+$-containing subphase at pH 12.9 and 0.5 ionic strength. $\pi$-A isotherms for a specific alkali metal cation converged and coincided in their low pressure-expanded regions when the pH of the subphase was varied at constant ionic strength (Fig. 2). At pH 10 and above, expanded portions of the $\pi$-A isotherms on 1.0 ionic strength subphases generated lower surface pressures than $\pi$-A isotherms on 0.1 ionic strength subphases (Fig. 2). These data confirmed and extended the results of Goddard et al. (3, 4) with strongly alkaline subphases. Small variations with pH in the low pressure-expanded regions of the isotherms which were noted by Rosano et al. (5) were not found in the present work (Fig. 2); however, experimental conditions were not identical in the two studies.

The Na$^+$ cation generally condensed the $\pi$-A isotherm and lowered the surface pressure of the phase transformation more than the K$^+$ cation at the same pH and ionic strength (Fig. 2). The Na$^+$ > K$^+$ condensing effect at pH 10 is shown with an expanded scale in Fig. 3. This cation selectivity sequence was not altered in the pH 10–12.8 range on either 0.1 or 1.0 ionic strength subphases.

At pH 9, 0.1 ionic strength, and very low surface pressures, monolayers spread on Na$^+$ and K$^+$ buffers were in a transitional state in which K$^+$ tended to condense the isotherm slightly more than Na$^+$ (Fig. 4). $\pi$-A isotherms were markedly expanded when the ionic strength at pH 9 was increased to 1.0 and a plateau was formed in the isotherm (Fig. 2). Under these conditions, K$^+$ condensed the isotherm and decreased the surface pressure of the plateau more than Na$^+$ (Fig. 4). This
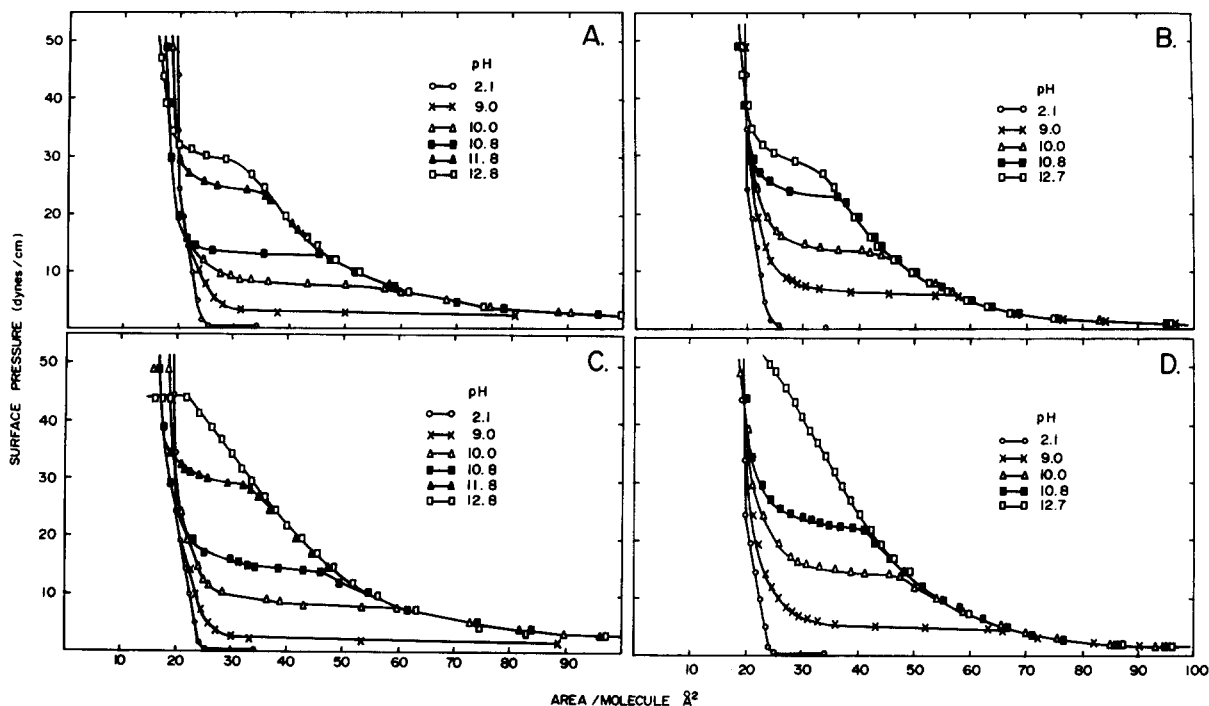
FIG. 2. $\pi$-A isotherms for stearic acid spread on subphases that contained Na$^+$ or K$^+$ cations and varied in pH and ionic strength. The cation and ionic strength were: *A*, Na$^+$ and 0.1; *B*, Na$^+$ and 1.0; *C*, K$^+$ and 0.1; *D*, K$^+$ and 1.0. Bicarbonate–carbonate buffers were used from pH 9 to pH 10.8. Data represent mean values from seven isotherms.
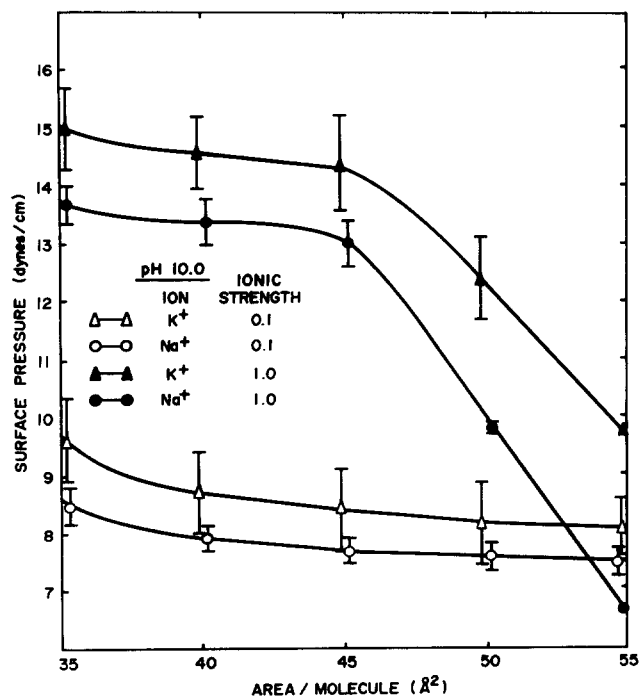


FIG. 3. Plateau regions of $\pi$-A isotherms at pH 10 (Fig. 2) on an expanded scale. Data represent means ± SD for seven isotherms.

reversal in cation affinity supported the observation of Sears and Schulman (2) of a K$^+$ > Na$^+$ reversal with the decrease in subphase pH obtained on 0.5 M bicarbonate subsolutions at pH 8.5.

### Condensing effect of neutral molecules on ionized films

The shielding effect of unionized stearic acid on film expansion which was first suggested by Rosano et al. (5) was studied by simulating partially ionized films with stearate–stearyl alcohol mixtures spread on 1.0 ionic strength subphases at pH 12.7. Stearyl alcohol had a significant condensing effect on these mixtures and very little film expansion occurred when the mole fraction of stearyl alcohol in the mixture exceeded 0.5 (Fig. 5).

Stearate films were unstable and desorbed slightly at high surface pressures on 0.1 ionic strength subphases (Fig. 2, *A* and *C*). The surface area, *A*, at constant surface pressure was therefore measured as a function of time, *t*, with stearic acid–stearyl alcohol mixtures spread on 0.1 ionic strength subphases at pH 12.8. The initial surface area of the mixture was then extrapolated from the relationship described by Ter Minassian-Saraga (12) for desorbing monolayers, in which the parameter $K_t$ is defined as:

$$d \log A/d\sqrt{t} = K_t \qquad \text{Eq. 1}$$

Surface areas were extrapolated at surface pressures where the stearic acid film was completely expanded and presumably ionization was effectively complete (Fig. 2, *A*). The extrapolated surface areas confirmed the condensing effect of stearyl alcohol on the mixtures
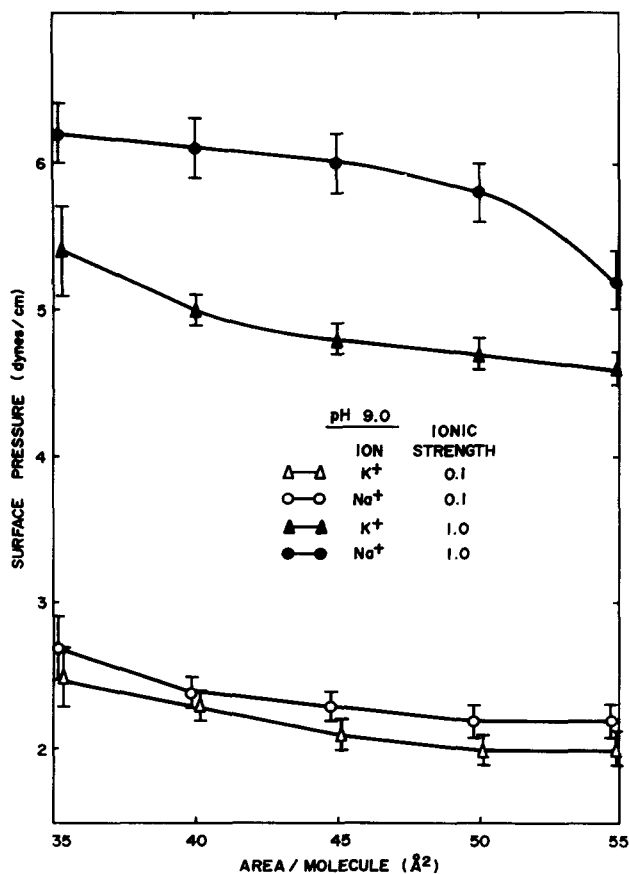
FIG. 4. Plateau regions of $\pi$-A isotherms at pH 9 (Fig. 2) on an expanded scale. Data represent means $\pm$ SD for seven isotherms at 0.1 ionic strength and 16 isotherms at 1.0 ionic strength.
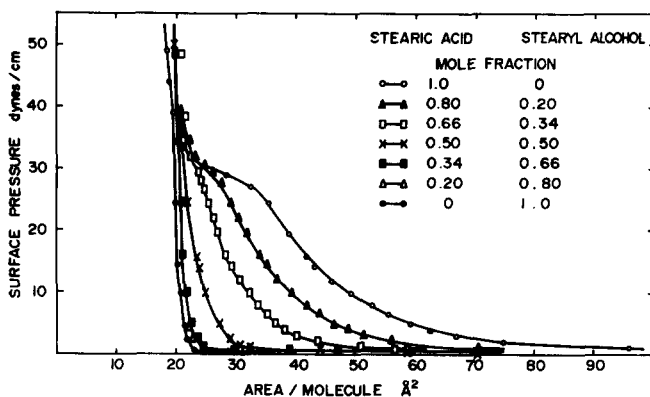


FIG. 5. $\pi$-A isotherms for stearic acid–stearyl alcohol mixtures spread on a pH 12.7 and 1.0 ionic strength subphase containing Na$^+$ (0.1 N sodium hydroxide and 0.9 M sodium chloride).
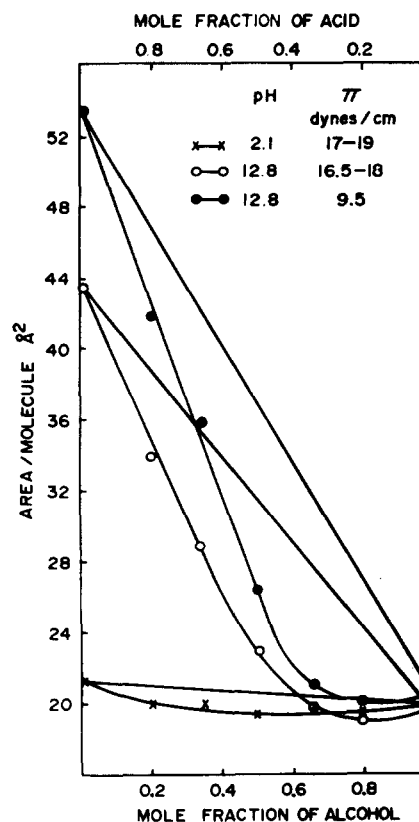


FIG. 6. Surface areas for stearic acid–stearyl alcohol mixtures extrapolated from desorption kinetic data for films spread on a pH 12.8 and 0.1 ionic strength subphase containing Na$^+$ (0.1 N sodium hydroxide). Surface areas for stable stearic acid–stearyl alcohol mixtures spread on a pH 2.1 subphase (0.01 N hydrochloric acid and 0.1 M sodium chloride) are included for comparison.

## DISCUSSION

$\pi$-A isotherms of fatty acids on alkaline subphases generally contain three distinct regions. They are expanded at low surface pressures, pass through a plateau or phase transformation during compression, and then approach the condensed state of an unionized monolayer (Fig. 2). Other investigators (2–5) have suggested that ionization was effectively complete in the expanded region of the isotherm and that ionization was incomplete in the plateau region of the isotherm. They proposed that the increased surface potential which developed during compression decreased surface pH and consequently the degree of ionization in the monolayer. A number of our experimental observations support this description of the $\pi$-A isotherm.

### The expanded region of the $\pi$-A isotherm

For completely ionized monolayers spread on a subphase containing a uniunivalent electrolyte, the repulsive pressure, $\pi_r$, is expressed by the Davies equation (13):

$$\pi_r = 6.1\sqrt{c}\,[\cosh\,\sinh^{-1}\,(134/A\sqrt{c}) - 1] \quad \text{Eq. 2}$$

(Fig. 6). Furthermore, extrapolated surface areas (Fig. 6) were similar to surface areas obtained from $\pi$-A isotherms (Fig. 2, $A$), indicating that desorption was not a significant problem at these surface pressures when the compression rate was 15 Å$^2$/molecule/min.

where $A$ is the area per molecule and $c$ is the ionic strength. The Davies equation predicts that surface pressure in completely ionized monolayers is independent of subphase pH and varies inversely with ionic strength. Since these predictions were confirmed in the expanded regions of $\pi$-A isotherms for monolayers spread on pH 10 or greater sodium chloride and potassium chloride subphases at 0.1 and 1.0 ionic strengths (Fig. 2), it was apparent that ionization was essentially complete in the expanded region of the isotherm.

### The plateau region of the $\pi$-A isotherm

For partially ionized monolayers spread on a subphase containing a uniunivalent electrolyte, the repulsive pressure, $\pi_r$, is expressed by (13):

$$\pi_r = 6.1\sqrt{c}\ [\cosh \sinh^{-1}(134\alpha/A\sqrt{c}) - 1]\quad \text{Eq. 3}$$

where $\alpha$ is the degree of ionization in the monolayer. $\alpha$ varies directly with pH, and since an increase in ionic strength lowers the surface potential, $\alpha$ also varies directly with ionic strength (14). Thus $\pi$ in partially ionized films will vary directly with both pH and ionic strength. Since these predictions were confirmed in the plateau regions of $\pi$-A isotherms for monolayers spread on pH 9–11.8 sodium chloride and potassium chloride subphases at 0.1 and 1.0 ionic strengths (Figs. 2–4), it was apparent that ionization was only partial in the plateau region of the isotherm.

Studies with the neutral molecule, stearyl alcohol, also support the concept that a surface film is partially ionized in the plateau region of the $\pi$-A isotherm. Stearyl alcohol condensed an expanded ionized stearate monolayer, and indeed the monolayer approached the condensed state as the mole ratio of stearyl alcohol to ionized stearate in the monolayer approached 1 (Figs. 5 and 6). A decrease in ionization during compression would increase the relative amount of unionized stearic acid in a partially ionized monolayer, and the increasing condensing effect of these neutral molecules would generate the plateau which was observed during compression. Stearic acid could have an even larger condensing effect than stearyl alcohol since stearic acid could not only shield the charged stearate molecules from each other but could also form condensed acid soaps (15, 16) with the charged stearate molecules.

### Counter ion selectivity

One limitation of the Davies (13) equation is that all monovalent ions are regarded as equivalent. Strong anionic fields of minerals, colloids, resins, glass electrodes, and biological membranes lead to cation selectivity sequences in which Na$^+$ interacts more strongly than K$^+$, whereas weaker anionic fields reverse this cation selectivity sequence (6, 7). Our results showed that stearate monolayers at pH 10 and above generated a strong anionic field since Na$^+$ condensed the film and lowered the surface pressure more than K$^+$ (Figs. 2 and 3). The condensing effect of the Na$^+$ cation was most apparent at pH 12.7–12.8, where a plateau appeared in isotherms generated on Na$^+$-containing subphases at both 0.1 and 1.0 ionic strengths but appeared in the isotherm generated on K$^+$-containing subphases at 0.1 ionic strength only (Fig. 2).

Eisenman (6) found that increased concentrations of H$^+$ converted the strong-field surface in a glass electrode to a weak-field surface with fewer charged groups. The stearate monolayer behaved in the same manner, since binding affinities for Na$^+$ and K$^+$ were reversed at pH 9 and 1.0 ionic strength (Fig. 4). Large cations have a greater binding affinity than small cations with weak fields (6, 7), and at pH 9 the large Tris cation interacted strongly with the film surface, displacing protons even at low ionic strength (Fig. 1). The role of H$^+$ ions in converting the stearate monolayer from a strong field to a weak field was also suggested in other studies (1) where the strong-field condensing sequence, Ca$^{2+}$ > Mg$^{2+}$ > Sr$^{2+}$ > Ba$^{2+}$, for alkaline earth cations at pH 9 was altered to a weak-field condensing sequence, Ba$^{2+}$ > Sr$^{2+}$ > Ca$^{2+}$ > Mg$^{2+}$, at pH 6.

The charge density in an ionizing fatty acid monolayer is readily varied by changing surface pressure, subphase pH, and subphase ionic strength, and by preparing mixed films of neutral and charged molecules. We suggest that further studies with these well-defined surfaces will provide additional information about cation binding in strong-field and weak-field surfaces.

## REFERENCES

1. Deamer, D. W., D. W. Meek, and D. G. Cornwell. 1967. Properties, composition, and structure of stearic acid–stearate monolayers on alkaline earth solutions. *J. Lipid Res.* **8:** 255–263.
2. Sears, D. F., and J. H. Schulman. 1964. Influence of water structures on the surface pressure, surface potential, and area of soap monolayers of lithium, sodium, potassium, and calcium. *J. Phys. Chem.* **68:** 3529–3534.
3. Goddard, E. D., S. R. Smith, and O. Kao. 1966. Monolayer properties of fatty acids. II. Behenic acid. *J. Colloid Interface Sci.* **21:** 320–330.
4. Goddard, E. D., O. Kao, and H. C. Kung. 1967. Monolayer properties of fatty acids. IV. Influence of cation at high pH. *J. Colloid Interface Sci.* **24:** 297–309.
5. Rosano, H. L., A. P. Christodoulou, and M. E. Feinstein. 1969. Competition of cations at charged micelle and monolayer interfaces. *J. Colloid Interface Sci.* **29:** 335–344.

6. Eisenman, G. 1962. Cation selective glass electrodes and their mode of operation. *Biophys. J.* **2**(**Part 2**): 259–323.
7. Diamond, J. M., and E. M. Wright. 1969. Biological membranes: the physical basis of ion and nonelectrolyte selectivity. *Annu. Rev. Physiol.* **31**: 581–646.
8. Shah, D. O. 1970. The effect of buffer ions on stearic acid monolayers in relation to foam stability. *J. Colloid Interface Sci.* **32**: 570–576.
9. Heikkila, R. E., C. N. Kwong, and D. G. Cornwell. 1970. Stability of fatty acid monolayers and the relationship between equilibrium spreading pressure, phase transformations, and polymorphic crystal forms. *J. Lipid Res.* **11**: 190–194.
10. Heikkila, R. E., D. W. Deamer, and D. G. Cornwell. 1970. Solution of fatty acids from monolayers spread at the air–water interface: identification of phase transformations and the estimation of surface charge. *J. Lipid Res.* **11**: 195–200.
11. Long, C. 1961. Biochemists' Handbook. Van Nostrand, New York.
12. Ter Minassian-Saraga, L. 1955. Etudes de l'adsorption et de la désorption aux surfaces liquides. *J. Chim. Phys.* **52**: 181–200.
13. Davies, J. T., and E. K. Rideal. 1963. Interfacial Phenomena. Academic Press, New York.
14. Payens, T. A. J. 1955. Ionized monolayers. Philips Res. Rep. **10**: 425–481.
15. Goddard, E. D., and J. A. Ackilli. 1963. Monolayer properties of fatty acids. *J. Colloid Sci.* **18**: 585–595.
16. Goddard, E. D., S. Goldwasser, G. Goliken, and H. C. Kung. 1968. Molecular association in fatty acid–potassium soap systems. *Advan. Chem. Ser.* **84**: 67–77.