Properties, composition, and structure of stearic acid–stearate monolayers on alkaline earth solutions

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ABSTRACT Interactions between alkaline earth ions and the carboxylate ligand in a stearic acid surface film have been investigated by IR spectrophotometry and surface chemical procedures. The frequency and shape of the carboxylate absorption band and the effect of hydration and pH on band characteristics suggest that beryllium, magnesium, and calcium ions form calcium-type complexes with the stearate ligand while strontium and barium ions form both calcium-type complexes and more ionic barium-type complexes, which have lower carboxylate band maxima.

Since IR band frequencies in anhydrous calcium-type complexes are directly proportional to the charge/(crystal radius) ratio, it is apparent that covalency decreases in the order: Be > Mg > Ca > Sr > Ba. The decreasing order of stability constants estimated from spectrophotometric titration data, Be > Ca > Mg > Sr > Ba, demonstrates that calcium behaves anomalously. This anomalous behavior is also apparent in the high solid-to-liquid phase transition temperature and small surface area of the calcium–carboxylate film compared to films composed of complexes with the other ions. A geometric factor related to the ionic radius and the radius of the carboxylate binding site formed by a calcium stearate lattice is proposed to explain the unique properties of calcium–carboxylate surface films.

Although the beryllium complex has the highest carboxylate band frequency and stability constant, it gives an atypical "expanded" surface film. A hydrogen bonded lattice formed with a soluble beryllium monohydrate is suggested as an explanation for this film property.

KEY WORDS monolayer · calcium · magnesium · alkaline earths · fatty acid · metal–carboxylate complex · IR spectra · hydration · stability constant · transition temperature · surface area · copolymeric lattice · binding site · ionic radius · pKa

CALCIUM AND BARIUM IONS strongly affect the properties of stearate monolayers; they condense the film and greatly increase its viscosity. These modifications in sur-face properties, which were first noted by Langmuir and Schaefer (1), have recently been explained by the formation of a lattice structure between the calcium ion and the oxygen atoms supplied by four equivalent carboxylate ligands (2). The calcium stearate lattice depends on the concentration of metallic ions in the film and has highly specific steric requirements (2). Solid condensed films will not form at a low pH where much of the fatty acid exists as the protonated species. Competition between hydrogen and metal ions was shown initially by Langmuir and Schaefer (3), who found that the concentration of metal ions in the monolayer increased with increasing pH. Similar pH effects were obtained by Havinga (4), Sobotka, Demeny, and Chanley (5), and Kimizuka and Koketsu (6). Experiments on steric requirements for the lattice structure have been limited to variations in the length, degree of saturation, and branching of the hydrocarbon chain used for the fatty acid film. These studies have shown, for example, that rigid films are formed only with saturated fatty acids that have a relatively small cross-sectional area, such as palmitic or stearic acid (2).

Interactions of alkaline earth metals with surface films have not been studied extensively. Experimental observations are generally limited to calcium even though beryllium, magnesium, calcium, strontium, and barium all react with fatty acid monolayers. Since the charge density and covalency of the metal and the geometry of the ligand molecule all affect stability constants for soluble chelates of the alkaline earth metals (7), it is probable that these properties affect metal–carboxylate complexes in surface films. We have employed IR spectrophotometry in a structural investigation of interactions of carboxylate films with the alkaline earth metals. This technique has been used by several investigators in related studies. Koga and Matuura (8) examined the structure of metal–carboxylate complexes in

solid soaps; Bagg, Abramson, Fichman, Haber, and Gregor (9) later studied calcium–carboxylate interactions in stearic acid monolayers; and Ellis and Pauley (10) characterized stearate multilayers that contained a variety of cations, including calcium and barium. The structural information obtained in our IR studies has been correlated with surface properties expressed through force–area isotherms and phase transition temperatures (2). These data suggest models and provide explanations for the film properties of the different alkaline earth complexes and, in particular, for the anomalous behavior of magnesium and calcium that was observed in the present study.

MATERIALS AND METHODS

Materials

Stearic acid was prepared in this laboratory and showed no impurities when analyzed as the methyl ester by gas–liquid chromatography. n-Hexane was washed with concentrated sulfuric acid and distilled at 69°C. Alkaline earth salts were A.R. grade; all were chlorides except for the beryllium salt, which was the sulfate. Water was distilled from glass into polyethylene containers. It had a specific conductance of 1.4×10^{-6} ohm^{-1}.

IR Analysis of Skimmed Films

A Langmuir trough, inner dimensions $1 \times 10 \times 50$ cm, was milled from a solid Teflon block. This trough was filled with 500 ml of a 0.2 mM alkaline earth solution. The pH was adjusted with 0.1 N NaOH or 0.1 N HCl and monitored during the experiment with a Corning Model 12 pH meter. Stearic acid, 0.4 mg/ml in hexane, was spread on the trough and the area/molecule was adjusted to near 20 A². The film was allowed to stand for 10 min and then compressed to the end of the trough where it was skimmed off onto 40 mesh wire gauze. The stainless steel gauze was rectangular and measured 1×2 cm. From three to five films were skimmed onto the gauze, which was then dried for several hours at room temperature before storage in glass vials. A number of skimmed films were dried over P_2O_5 at room temperature for 1–4 days. Spectra were obtained on the same sample before and after drying.

Absorption spectra were obtained by placing the gauze in the sample beam of a Beckman IR 9 spectrophotometer. Expanded scale spectra were recorded from 1400 to 1800 cm^{-1} and 2700 to 3100 cm^{-1}. The metal–carboxylate content of the film was estimated by the procedure described by Bagg et al. (9). The absorbancy for the antisymmetric (2920 cm^{-1}) C–H stretching band, A_{CH}, was divided by either the carboxylate absorbance, A_{COO^-}, in the completely ionized film or the carbonyl absorbance,

$A_{C=O}$, in the completely protonated film to yield relative intensity coefficients C_{COO^-} and $C_{C=O}$.

These coefficients were then used in the quantitative analysis of spectra obtained with mixed carboxylate–carboxylic acid films. When split carboxylate peaks occurred, the two absorbancies were added together and the average was taken. Absorbance data and integrated data were compared in one series of experiments. The integrated area was calculated as the half-band width multiplied by the absorbance (11).

Surface Pressure

Surface pressure, π, was measured by the Wilhelmy plate technique (12) with the use of the Teflon trough described above. The dipping plate was a square of platinum foil 2.54 cm wide. The apparatus was enclosed in a vinyl plastic case and all measurements were made at 26–28°C.

Phase Transition Temperature

Solid-to-liquid phase transition temperatures were compared by the Devaux talc test (2). A monolayer was formed on 1 liter of subphase placed in a Pyrex dish 14.5 cm in diameter. The fatty acid solution in hexane was spread slowly until a lens formed and the resulting monolayer was detected by a light sprinkling of talc. A small jet of air was directed on the film and the dish was heated until particle movement was observed. The transition was considered complete only when all the talc particles were in motion and no "islands" of solid film remained. A transition temperature could not be determined for either beryllium soap films or calcium and barium soap films in the upper pH range, since the film remained in solid islands even near the boiling point of water. However, other transition temperatures were below 90°C, and were reproducible over a range of 5–10°C.

RESULTS

IR Spectra of Metal–Carboxylate Complexes

Frequency maxima for metal–carboxylate absorption bands obtained with the different alkaline earth metals are recorded in Table 1. Only metal–carboxylate bands appeared in the spectra of films that had been skimmed at high pH. Both metal–carboxylate and carboxylic acid (1698–1710 cm^{-1}) bands appeared in the spectra of films obtained at intermediate pH values. Carboxylate bands, COO$^-$, disappeared at low pH, where a typical unionized carboxylic acid (COOH) spectrum occurred (see below, Fig. 3).

Spectra for alkaline earth complexes sometimes showed single carboxylate peaks and at other times showed split carboxylate peaks. The frequency and shape of the carboxylate band and the effect of hydration and pH on

TABLE 1. IR ABSORPTION MAXIMA FOR THE STEARATE CARBOXYLATE FREQUENCY IN THE PRESENCE OF ALKALINE EARTH AND SODIUM IONS

Ion and pH		COO⁻ Antisymmetric Stretching Band	
		Wet	Dry
		cm^{-1}	
Be⁺⁺	5.6	1567	—
	4.4	1567	—
Mg⁺⁺	9.0	1540, 1580*	—
	8.4	—	1588
	6.5	1540, 1578*	—
Ca⁺⁺	8.8	1540, 1580*	1583
	6.7	1540, 1580*	1583
Sr⁺⁺	9.0	1525, 1565*	1516, 1577*
	7.2	1540, 1570*	1578
Ba⁺⁺	8.7	1512	—
	8.3	1512	1512
	7.3	1512, 1575*	1512, 1575*
	6.6	1575	—
Na⁺	9.0	1540, 1577*	1583

* Two maxima of a split carboxylate peak.

band characteristics suggested that two types of metal–ligand complexes, the calcium-type and the barium-type, occurred with the alkaline earth ions. Calcium stearate complexes exhibited a split carboxylate peak which was converted to the higher frequency peak when the film was dried (Figs. 1 and 2). Similar data were obtained by Bagg et al. (9) for wet and dried calcium stearate. Magnesium and beryllium ions also formed calcium-type complexes (Table 1). Wet or partially dried magnesium stearate films had a broad split carboxylate peak, which was converted to the broad higher frequency band when
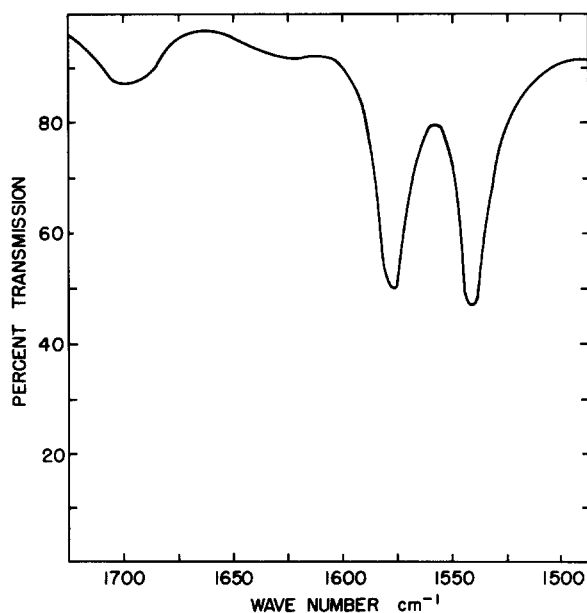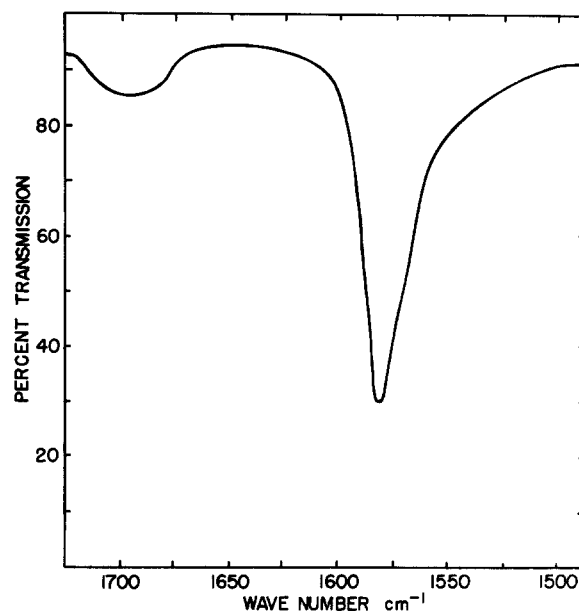

FIG. 2. IR spectrum of the calcium stearate film shown in Fig. 1 after it had been dried over P_2O_5 for 96 hr.

the film was dried. Wet beryllium stearate complexes showed only one carboxylate band in this study; however, this 1567 cm⁻¹ band corresponded to the lower frequency peak in the split carboxylate spectrum obtained for beryllium stearate by Koga and Matuura (8) and probably represented the fully hydrated species.

Both wet and dried barium stearate complexes skimmed from subsolutions at pH 8.3 and 8.7 had a sharp carboxylate peak (Table 1). Wet and dried barium stearate complexes skimmed from subsolutions at pH 7.3 and 7.9 had a split carboxylate peak. A barium stearate complex skimmed at pH 6.6 showed only the higher frequency peak. The split peak and the frequency shift in this series were apparently related to pH rather than hydration, which was the important factor in band characteristics for calcium-type complexes. Similar results were obtained by Francis and Ellison (13), who found that the 1512 cm⁻¹ carboxylate band for barium stearate films deposited on a CaF_2 plate was converted to a 1552 cm⁻¹ band when the film was deposited from a subsolution at pH 7.5.

Strontium stearate films appeared to have structures that were intermediate between the barium-type and calcium-type films. Wet strontium stearate skimmed at pH 9 had a broad split peak which was converted to a sharp, but still split, peak when the film was dried; films dried for as long as 96 hr still retained a split carboxylate band. The intensity of the higher frequency peak in the split carboxylate spectrum increased as the pH of the subsolution was lowered, and the lower frequency band tended to disappear near pH 7. Thus the carboxylate

FIG. 1. IR spectrum of a calcium stearate–stearic acid film skimmed from a pH 6.7 subphase containing 0.2 mM CaCl₂. The film was air-dried.

band in strontium stearate films was altered by both pH and hydration.

Monolayer Composition

IR spectra of monolayers formed over subphases in an intermediate pH range showed both carboxylate and carboxylic acid absorption bands. Absorbance values $A_{C=O}$ and A_{COO^-} were corrected with intensity coefficients $C_{C=O}$ and C_{COO^-} in order to calculate the stearate concentration.

Stearate in mole $\%$ =

$$100\ C_{COO^-}\ A_{COO^-}/(C_{COO^-}\ A_{COO^-}\ +\ C_{C=O}\ A_{C=O})$$

The relative intensity coefficient of the carbonyl band (relative to C–H) varied from 2.0 to 2.6 in experiments where unionized stearic acid was skimmed from subsolutions containing magnesium, calcium, strontium, and barium ions. The value 2.4 which was used in this study is similar to the coefficient of 2.0 calculated by Bagg et al. (9). When stearic acid was skimmed from a subsolution containing beryllium ions, the coefficient was 3.8. This coefficient, which suggests an interaction between the carboxylic acid and a beryllium hydrate, was used in calculating the stearate content of beryllium stearate films.

Carboxylate band intensities differed for different metals and for anhydrous and partially hydrated complexes. Relative intensity is inversely proportional to absorbance and therefore related to the shape of the band. Broad split peaks had lower absorbancies at the band maxima than sharp split peaks. The absorbance for a single sharp peak was greater than the average absorbance for split peaks. Coefficients were calculated from a completely ionized film in each experimental series, and these coefficients were then used in estimating the stearate content of films in that series. The shape of the carboxylate peak was usually similar for completely ionized and partially ionized films in a specific experimental series. However, barium stearate complexes had a single carboxylate peak in the high pH region and a split carboxylate peak at low pH, and the relative intensity of the higher frequency band in strontium stearate complexes increased somewhat as the pH was lowered. Sharp peaks for beryllium, dried calcium, and barium stearate complexes gave intensity coefficients of 1.5, 1.0, and 1.2, respectively. The intensity coefficient for the split carboxylate peak in a partially hydrated calcium stearate film was 1.5. Magnesium and strontium complexes gave broad split carboxylate peaks which had relative intensity coefficients of 4.2 and 3.4 respectively. Partially dried strontium complexes had much sharper split carboxylate peaks and a relative intensity coefficient of 1.9.

Intensity coefficients calculated from integrated area data were different from the coefficients calculated from
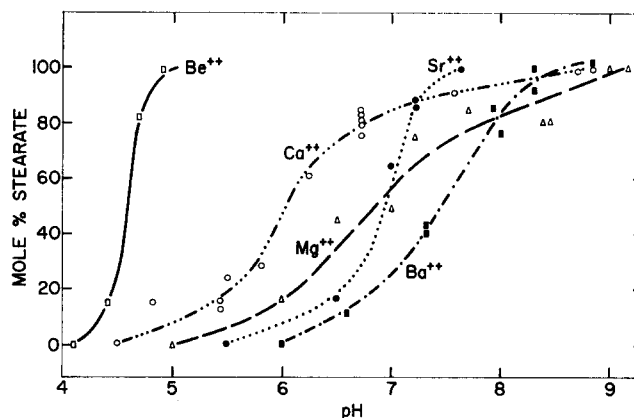

FIG. 3. Stearate content, determined by IR spectrometry, of monolayers layered over different alkaline earth ions, plotted against pH. The alkaline earth ion concentration was 0.2 mM in all subphases.

absorbance data alone. With integrated areas, the relative carbonyl intensity was 0.52 and the relative carboxylate intensity for a dried calcium stearate complex was 0.55.

The stearate content of skimmed monolayers is a function of both pH and the alkaline earth ion present in the subphase (Fig. 3). Thus the apparent pKa of stearic acid was 4.6 with beryllium, 6.0 with calcium, 6.8 with magnesium, 6.9 with strontium, and 7.5 with barium. Absorbance and integrated area methods gave a similar stearate content for one series of films skimmed from calcium subphases. The apparent pKa values in this series were 6.2 with absorbance data and 6.0 with integrated area data. These results are in agreement with the few data in the literature. Bagg et al. (9) found the same apparent pKa, 6.0, for stearic acid on a calcium ion subphase. Langmuir and Schaefer (3) observed in their early studies that fatty acid films spread on barium had a higher pKa than films spread on calcium subphases.

Phase Transition Temperature

Fig. 4 summarizes the data for phase transition temperatures that were obtained when stearic acid was spread over magnesium, calcium, strontium, and barium subphases. It is apparent that transition temperature depends on both pH and on the specific alkaline earth ion. Thus transition temperatures were higher in the alkaline pH range, where the film existed largely as a metal–carboxylate complex (Fig. 3). The transition temperature tended to increase with increasing atomic number, although calcium values were anomalous. Barium complexes always had a higher transition temperature than magnesium and strontium complexes, and the barium complex had a higher transition temperature than the calcium complex at pH 6, even though IR data (Fig. 3)
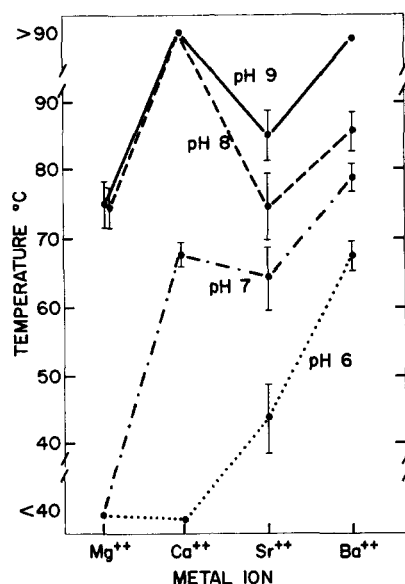
FIG. 4. Phase transition temperatures for stearic acid monolayers layered over subphases containing different alkaline earth ions (0.2 mM) at the specified pH.

suggested that barium did not form a carboxylate complex in this pH region. The most striking aspect of these experiments was found in the anomalous behavior of the calcium–stearate complexes, which had transition temperatures higher than other alkaline earth complexes in the pH 8–9 region.

Beryllium was not included in this series since a visible precipitate, presumably a complex beryllium hydroxide (14), formed at pH 7.5 and above. However, films on beryllium were very rigid and did not melt in the pH 5–9 region even when the subphase was turbid and the beryllium ion was obviously precipitated, in part, as a hydroxide.

Surface Area

Force–area data are summarized in Figs. 5–7 for stearic acid spread on magnesium, calcium, strontium, and barium subphases at different hydrogen ion concentrations. Calcium had an atypical effect on the cross-sectional area of stearic acid. Other alkaline earth ions condensed the film somewhat but did not yield the solid condensed force–area curve found with calcium stearate (Fig. 5). The condensing effect of alkaline earth ions—except for calcium—decreased with increasing atomic number in films in which the carboxylic acid group was completely ionized (Fig. 5). Thus, the condensing effect sequence at pH 9 was: Ca > Mg > Sr > Ba. It is interesting that both transition temperature and condensing effect were higher than expected with calcium at this pH. The converse occurred at pH 6, where the condensing effect decreased with decreasing atomic number in the sequence: Ba > Sr > Ca > Mg (Fig. 7). Calcium as-

sumed its expected place in the alkaline earth sequence at this pH. The interaction of magnesium with the film was the one most susceptible to a change in pH; magnesium had little effect on the cross-sectional area of a stearic acid film at pH 7.5 (Fig. 6) even though it had a pronounced condensing effect at pH 9.

Force–area data are summarized in Fig. 8 for stearic acid spread on the beryllium subphase at pH 6 and 7.5, in the pH region where a visible beryllium hydroxide precipitate was not formed. Force–area curves for beryl-
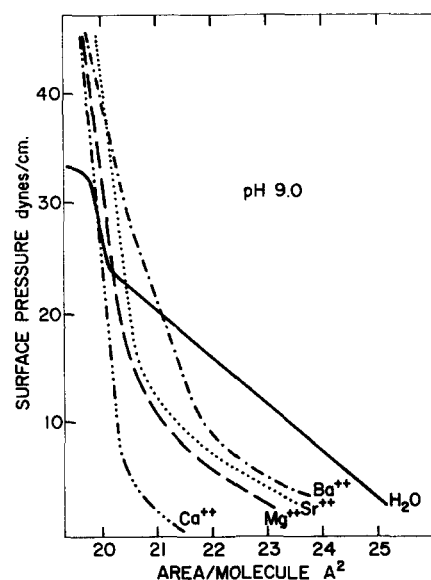

FIG. 5. Force–area curves for stearic acid monolayers layered over subphases containing different alkaline earth ions (0.2 mM) at pH 9. The "H₂O" curve is for pure water.
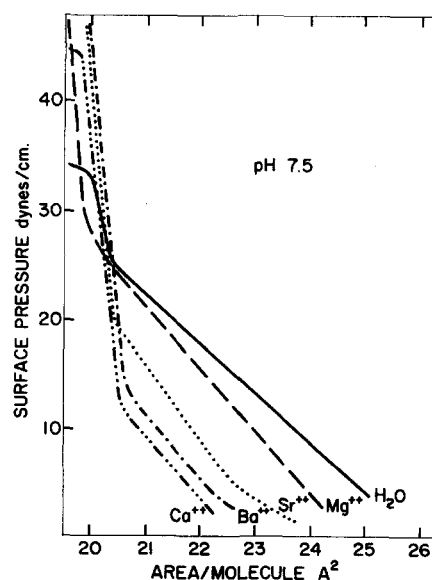

FIG. 6. Force–area curves for stearic acid monolayers layered over subphases containing different alkaline earth ions (0.2 mM) at pH 7.5.
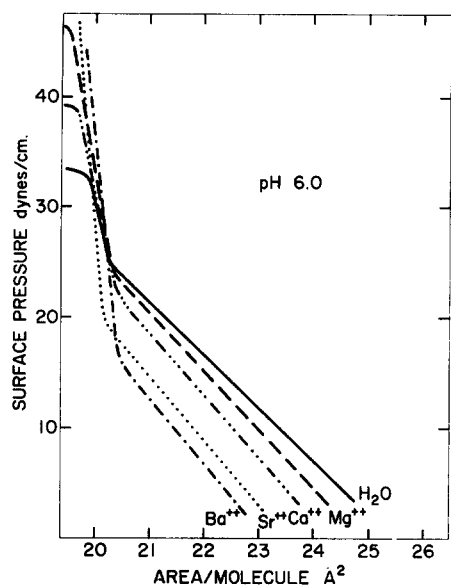
Fig. 7. Force–area curves for stearic acid monolayers layered over subphases containing different alkaline earth ions (0.2 mM) at pH 6.0.
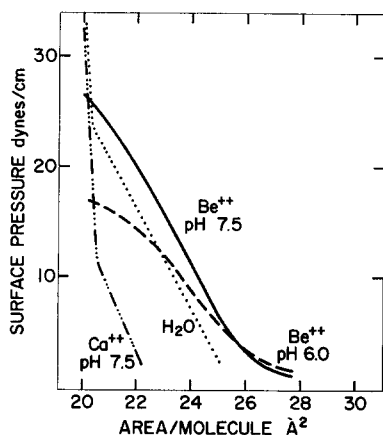

Fig. 8. Force–area curves for stearic acid monolayers layered over subphases containing 0.2 mM beryllium sulfate adjusted to pH 6 and pH 7.5. Force–area curves for pure water and a subphase containing the calcium ion at pH 7.5 are included for comparison.

lium could not be reproduced as well as curves obtained with other ions. However, it was evident that beryllium expanded rather than condensed the film in this pH region—even though stearic acid was converted completely to beryllium stearate at pH 5 and above (Fig. 3). The curve shown in Fig. 8 is compared with that for a monolayer on pure water (the concentration of Na$^+$ ions in the beryllium experiments was negligible, and Na$^+$ at 0.2 mM does not expand the film).

DISCUSSION

Unionized carboxylic acids show a typical absorbance at 1710 cm^{-1} which vanishes on ionization (8, 15, 16).

The usual carbonyl absorbance (1710 cm^{-1}) is replaced by the antisymmetric and symmetric C–O stretching vibrations of the COO$^-$ group at approximately 1550–1610 and 1300–1400 cm^{-1}, respectively. The higher energy band can be identified unambiguously and has been used in this study because the antisymmetric C–O stretching vibration depends in part on the metal ion associated with the carboxylate ligand. IR spectra suggest that the alkaline earth–stearate complexes exist in calcium-type and barium-type structures. This concept is supported by x-ray diffraction studies, which show that anhydrous barium stearate has a different crystal structure from either anhydrous or hydrated calcium stearate (8). We have assigned the lower frequency peak in the split carboxylate spectra of calcium-type complexes to a hydrated species. The carbonyl stretching frequency is lowered by hydrogen bonding (17), and this undoubtedly explains the frequency shift between anhydrous and hydrated complexes and the split bands in the 1540–1590 cm^{-1} IR region. The effect of hydrogen bonding is apparent from the spectra in Figs. 1 and 2. A calcium stearate film dried in air possessed two strong absorptions, at 1540 and 1580 cm^{-1}. After drying in vacuum over P$_2$O$_5$, the 1540 cm^{-1} peak completely disappeared and the other peak became sharper, with a maximum at 1583 cm^{-1}. The same behavior was also observed whenever a film of magnesium stearate (or, for that matter, sodium stearate) was thoroughly dried. Furthermore, calcium and magnesium complexes at intermediate pH values showed absorptions in the two spectral regions characteristic of water (3400 and 1650 cm^{-1}). The magnesium complex at pH 9.2 showed two strong absorptions at 3400 and 3300 cm^{-1}, which may indicate the possibility of OH$^-$ in addition to water. Split carboxylate peaks for calcium stearate and a broad carboxylate peak for magnesium stearate were observed in other studies (8–10, 13, 18). Ellis and Pyszora (18) and Koga and Matuura (8) did not assign the lower frequency band to a hydrated species although Koga and Matuura showed that this band largely disappeared when the complex was dried.

Barium-type complexes are apparently different from calcium-type complexes. A single carboxylate band in the 1512 cm^{-1} region was observed for barium complexes in this study and in several previous investigations (8, 10, 13, 18). Drying appeared to have no effect on the shape and frequency of the band. A higher frequency carboxylate band appeared in a split peak when the film was spread as a barium stearate–stearic acid mixture. Francis and Ellison (13) found a similar pH effect. They attribute the lower frequency band in the split carboxylate peak to a coupling between carboxylate ions that is destroyed when the carboxylate film is diluted with stearic acid. Since carboxylate spectra for strontium stearate are affected by both hydration and pH, this alkaline earth
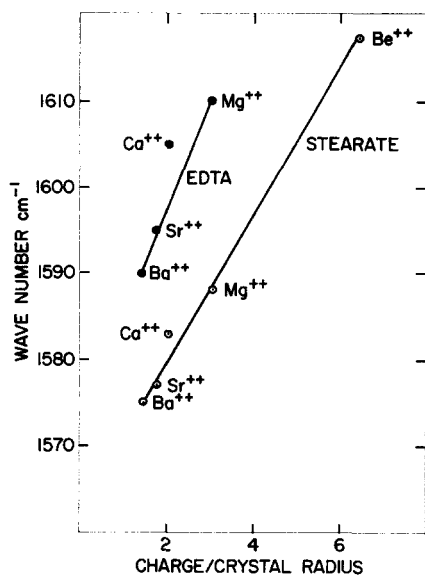
FIG. 9. The relationship between carboxylate maxima and the charge/(crystal radius) ratio for alkaline earth complexes with EDTA (19) and stearic acid.

ion may represent a transition between calcium-type and barium-type complexes. X-ray diffraction data indicate that anhydrous strontium and barium complexes are more closely related than anhydrous strontium and calcium complexes (8).

If we assign the higher frequency band obtained for beryllium stearate to the anhydrous complex (see Results), the band frequencies for calcium-type complexes decrease in the order: Be > Mg > Ca. This series corresponds to the series reported by Sawyer and Paulsen (19) for the frequency shift in alkaline earth–EDTA (ethylenediamine tetraacetate) complexes. Carboxylate maxima for anhydrous complexes of the calcium-type and the higher frequency bands in mixed stearic acid–strontium or calcium stearate films decrease with increasing size of the metal ion in the same way that band maxima for the corresponding alkaline earth–EDTA chelates decrease with increasing ionic size. This frequency series suggests that the barium-type complex is converted in part to the calcium-type complex. Indeed, a linear correlation exists between the carboxylate frequencies and the charge/(crystal radius) ratios of the metallic ions in both EDTA and stearate complexes (Fig. 9). The trend in carboxylate frequencies indicates an increase in the degree of covalent bonding as the ionic radius of the alkaline earth ion decreases. Furthermore, the data suggest that barium-type complexes are much more ionic than calcium-type complexes. Ellis and Pyszora (18) were unable to correlate frequency shifts for carboxylate groups with either electronegativity or the ionic radius of an alkaline earth metal; however,

these investigators attempted to correlate split carboxylate bands in calcium-type complexes with those in barium-type complexes.

A partial covalent character for the calcium–oxygen bond in calcium stearate monolayers has been suggested by several workers to account for certain properties of the film (9, 20, 21). In particular, partial covalent character is useful in explaining why calcium is more strongly bound than sodium (20). However, the frequency region (1512–1617 cm^{-1}) of IR absorption for alkaline earth and sodium complexes indicates that the bonding is primarily ionic in all the complexes.

The concentration of free ligand (carboxylate anion) in a stearic acid surface film is a function of the stability constant of the metal chelate. On the assumption that the binding of the alkaline earth cation does not alter the ionization of the remaining unionized carboxylic acid groups (22), variations in apparent pKa must reflect differences in the stability constants of the metal complexes. Complexes with larger stability constants will require higher hydrogen ion concentrations to displace the metal ion and these complexes will, therefore, have a lower apparent pKa. Thus IR data indicate that stability constants are in the order: Be > Ca > Mg > Sr > Ba. Since the shape of the "titration" curve depends on the intensity coefficient chosen for the carboxylate band, and the absorbance data introduce uncertainty in the calculation of this coefficient, these titration curves and apparent pKa values are probably semiquantitative and indicate only the relative stability of the metal–carboxylate complexes. Electronegativity, ionic radius, and ionic potential data all predict that magnesium complexes should have larger stability constants than calcium complexes (7). The predicted regularity in binding order occurs with most carboxylate and phosphate ligands; however, the magnesium–calcium stability constant order is reversed in EDTA (7) and phosphatidic acid complexes (22), and the constants are equal with citrate (7) and a number of different phospholipid ligands (23).

Sawyer and Paulsen (19), and Abramson, Katzman, Gregor, and Curci (22) attribute the magnesium–calcium reversal to a tendency of magnesium to be more strongly hydrated in aqueous solutions. In fact, IR data with the EDTA ligand indicate that the anhydrous magnesium complex is more covalent than the calcium complex and should probably have a larger stability constant. Similar results were obtained in our study. The magnesium–calcium reversal in stearate films would not have been predicted from frequency maxima, which indicate that anhydrous magnesium stearate is more covalent than anhydrous calcium stearate. Carboxylate frequencies for the hydrated species were equal in calcium and magnesium stearates; however, frequency maxima obtained with split peaks are somewhat uncertain and these IR

measurements are not adequate for distinguishing the finer structural aspects of hydrated complexes.

Care and Stavely (24) attribute the anomalous order of stability constants for alkaline earth–EDTA complexes to a geometric factor; they suggest that calcium has the most favorable ionic radius for binding to the carboxylate ligand. Structural effects on binding order in alkaline earth complexes have been postulated in several other investigations which are summarized by Rubin (7). In a previous study (2), we suggested that the most probable structure for the calcium stearate film was a "copolymeric" lattice in which each calcium ion fitted a binding site consisting of four carboxylate oxygens. A scale drawing of the lattice with alkaline earth ions superimposed on the binding sites is presented in Fig. 10. Calcium readily superimposes on all four oxygens while the model suggests that magnesium may be too small for the binding site.

The type of lattice proposed has rigid steric requirements and cannot be formed with branched or unsaturated fatty acids (2). If the geometric factor introduced by a lattice explains in part the anomalous stability constant of the calcium complex, this complex should also exhibit surface properties that differ in some manner from the surface properties of alkaline earth complexes with less favorable geometric structures. Surface properties are indeed altered. The phase transition temperature for the calcium complex is considerably higher (at least at pH 7–9) than the transition temperature for either magnesium or strontium complexes, and
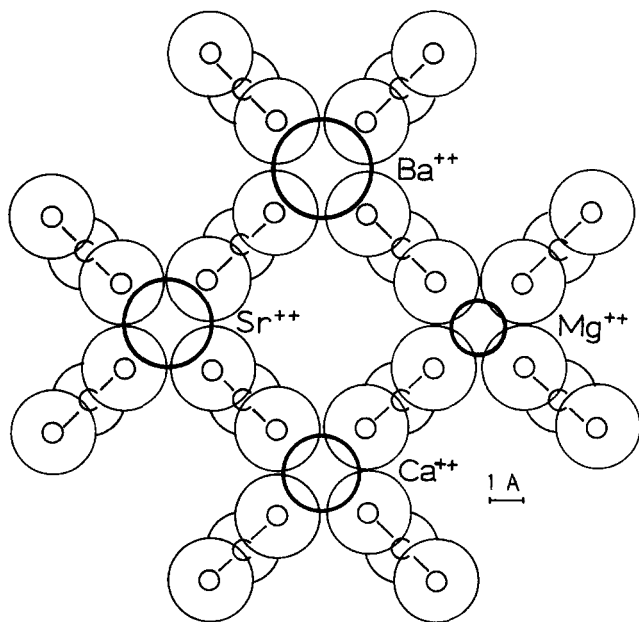
at low surface pressures calcium has a significantly greater condensing effect on the film than other alkaline earth ions.

The geometric factor introduced by a lattice structure may be tested in another way. If anomalous surface properties are related to the lattice structure, they will occur only at an elevated pH, a region where the film is completely ionized. The calcium effect in fact disappears at pH 6, a region where the film is largely protonated and only a few soap molecules are present. It is interesting that barium, the ion with the lowest stability constant, has the greatest effect on the phase transition temperature even though the barium stearate content of the skimmed film is the lowest of all alkaline earth complexes in this pH region. These data are consistent with the observation of Ellis and Pauley (10) that barium ions also complex with unionized carboxylic acids. Melting undoubtedly involves several anisotropic mesophase transitions within the hydrocarbon phase in addition to the final solid-to-liquid transition, which involves the ionic structure of the soap (16). The geometry of the calcium soap lattice may impart a unique stability to the surface film which is not obtained with other mesophases found in bulk phase soaps. Bulk phase melting, for example, does not show the anomalous calcium effect (25). The calcium–barium inversion at low pH may be explained by the absence of a unique lattice structure and a phase transition which now follows the typical bulk phase melting order: Mg < Ca < Ba (25). It should be emphasized that the structure of the hydrocarbon phase is also important in bulk phase melting. Thus barium laurate decomposes above 260°C while barium oleate decomposes at 100°C (25).

Beryllium, an atypical alkaline earth metal, has a large charge/radius ratio and generally forms compounds which are at least partially covalent (14). Beryllium carboxylates, for example, are soluble in nonpolar solvents and unionized in water (14). Covalency explains the strong bonding and large stability constant for beryllium stearate that is inferred from the carboxylate band frequency of hydrated beryllium stearate and the apparent pKa of stearic acid films layered over a beryllium-containing subphase. However, covalency does not explain all the properties of the beryllium stearate monolayer, particularly the "expanded" nature of its force–area curve. There is some evidence for the existence of soluble $[Be(OH)^+]_n$ species in aqueous solutions (14). These hydroxides may contribute to film properties by forming a hydrogen-bonded lattice structure with the carboxylate film. A similar structure has been suggested by Thomas and Schulman (26) for copper mono-soaps, which form very rigid films under similar conditions. The limiting area per molecule for the copper soap film, 28 $Å^2$, is related to the hydrogen-bond distance rather than the area occupied by the hydrocarbon chain, 20 $Å^2$. The

FIG. 10. Scale drawing showing a cross-section of the stearate copolymeric lattice with alkaline earth ions superimposed on typical binding sites.

beryllium soap film is also rigid and collapses before reaching the cross-sectional area of a hydrocarbon chain. The similarity in properties of the two films, together with the hydrogen-bonding possibilities for both copper and beryllium complex ions, strongly suggests that the unusual properties of their soap films arise from similar structures.

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