Two-Dimensional Surface Properties of 2-Methoxy Ethyl Oleate at the Air/Water Interface

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ABSTRACT: Methoxy ethyl oleate, a nonionic surfactant, has been investigated at the air/water interface for various surface properties by employing the Langmuir film balance technique. The ester forms an expanded isotherm at the air/water interface. The minimum area of packing (A_0), initial area of increase of surface pressure (A_i), collapse pressure (π_c), and area/molecule at collapse pressure (A_c) have been estimated from the isotherm curve. The higher compressibility coefficient (K) suggests that the ester forms a more expanded liquid film than the parent oleic acid. Besides, the ester film is fairly stable as suggested by only about 30% loss in area over a period of 20 min. The relaxation rates of the ester film at different surface pressures of 10, 15, and 20 $mN \cdot m^{-1}$ have been estimated from changes in the surface area/molecule with time. Interestingly, the surface area (54.2 $Å^2$/molecule) that corresponds to a minimized structure projected for the ester, calculated theoretically, agrees reasonably well with the experimental value (57.2 $Å^2$/molecule).

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KEY WORDS: Collapse pressure, compressibility coefficient, isotherm, Langmuir film balance, methoxy ethyl oleate, relaxation rate.

Fatty acids and their derivatives, such as esters and amines, exhibit surface activity by virtue of their amphipathic structures, and are capable of forming organized assemblies ranging from monolayers and micelles to membranes akin to classic surfactant materials (1,2). It is well known that the glyceryl esters of fatty acids form the main component of lipids present in cell membranes. Organized assemblies of fatty acids and their esters thus provide useful models for understanding various membrane-mediated processes (3–5). The orientation and conformation of surface-active molecules influence some important surface and interfacial properties, such as packing density, hydrophilicity, and free energy. The Langmuir film balance (LFB) technique provides a simple tool for drawing useful information that compares well with theoretical modeling studies (6). Extensive studies have been carried out on the monolayer properties of fatty acids with the LFB technique (7,8). The influence of pH and multivalent metallic ions present in the subphase on the packing of fatty acid molecules has been demonstrated in recent studies (9). It is inferred that trivalent ion, (Tb^{+3}), affects maximum condensation of stearic acid at the air/water interface. Among various fatty acids, unsaturated fatty acids, such as oleic and linoleic acids, assume immense significance owing to their tremendous potential in various formulations, such as corrosion inhibitors, extreme-pressure lubricants, pharmaceuticals, paints, food, and cosmetics. Furthermore, these fatty acids enable introduction of functional groups at the double bond through chemical modification processes, such as polymerization (10,11), sulfation, and chlorination (12). These unsaturated fatty acids and their derivatives can be considered as reactive surfactant systems, capable of promoting chemical reactions inside the respective organized assemblies. The advantages of such reactions in exhibiting control over the microstructure and molecular properties of the ultimate product have been well documented (13,14). To cite an example, polymerization inside aqueous micellar assemblies influences the polydispersity and microstructure of the homopolymer of methoxy poly(ethylene glycol) acrylate (15). To exploit the advantages of chemical reactions inside the organized assemblies involving oleic acid or its ester, it is necessary to investigate the surface properties in detail. The influence of the *cis* double bond on the organization behavior of oleic acid at the air/water interface has been reported in a few studies (16,17). In this study, 2-methoxy ethyl oleate has been selected because it has extended polar groups at the hydrophilic end. Some of the significant parameters pertaining to packing behavior of the tail group, orientation of the head group, and stability of the ester film at the air/water interface have been determined by the LFB technique.

EXPERIMENTAL PROCEDURES

Materials. Cis-octadecenoic acid (oleic acid), 98% pure, was purchased from Sigma Laboratories (St. Louis, MO), and 2-methoxy ethanol (99% pure) was from Glaxo Laboratories, India. Analar para-toluene sulfonic acid with a purity >98% (S.D. Fine, India) was used as catalyst in the synthesis of the ester. Chloroform used in the monolayer experiments was of high-performance liquid chromatography grade. Distilled water was purified with a Milli Q (Millipore, Milford, MA) filtering system for the monolayer experiments. The surface

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tension of Milli Q water was estimated at 72.6 mN·m^{-1} at 25°C, which agreed with the reported value within limits of experimental error.

Synthesis and characterization of 2-methoxy ethyl oleate. Oleic acid (28.2 g, 0.1 M) was reacted with 14 g (0.2 M) of 2-methoxy ethanol in the temperature range of 130–160°C with 0.1% para-toluene sulfonic acid as catalyst. The mixture was stirred throughout the reaction, and water formed from the reaction was continuously removed. The reaction went to about 85% completion as indicated by the acid value of the reaction mixture. The unreacted methoxy ethanol in the mixture was removed by vacuum distillation. The product was washed initially with 1% aqueous sodium bicarbonate solution, followed by 20% saline water to remove the catalyst and the unreacted fatty acid. The ester was extracted with ethyl acetate, followed by diethyl ether, and all solvent was removed by vacuum distillation. The isolated ester was characterized by chemical and spectroscopic analyses. Yield was 60%.

Acid value, ester value, and I_2 value were estimated by reported methods (18). The infrared spectrum was obtained from the neat film of the ester on sodium chloride crystal in a Nicolet DXB spectrometer (Madison, WI). ^{1}H and ^{13}C nuclear magnetic resonance (NMR) characterization of the ester was performed on a Bruker MSL 300P (300 MHz) (Karlsruhe, Germany) NMR spectrometer with $CDCl_3$ as the solvent. Tetramethyl silane was employed as the internal standard.

Measurements with Langmuir film balance. Surface pressure (π)-area (*A*) isotherm experiments were performed on a Nima Teflon®-coated Langmuir Trough (Model No. 61) (Nima Technology Ltd., United Kingdom). Typically, 50 µL of a chloroform solution of the ester in the concentration range of $0.118–17.6 \times 10^{-4}$ M was slowly spread on the water subphase. The compression was started 10 min after spreading, to allow complete evaporation of the solvent. A barrier speed of 50 cm^2/s was maintained. A Wilhelmy plate with a microprocessor-controlled film balance with a precision of 0.01 mN·m^{-1} has been employed. The water surface was cleaned by aspiration after each experiment. All measurements were carried out at a temperature of 25 ± 0.1°C. The absence of surface-active impurities in the solvent was confirmed by performing a blank run with the solvent. The π-*A* isotherm and hysteresis experiments were performed three times to check the reproducibility of results. The π-*A* isotherm experiments were performed as a function of concentration. The kinetics of relaxation of the monolayer film were estimated from the variation in molecular area with time at constant pressures of 10, 15, and 20 mN·m^{-1}. In such experiments, compression of the ester was performed 10 min after spreading, just up to the desired pressure, and then the change in area with time was followed by keeping π constant.

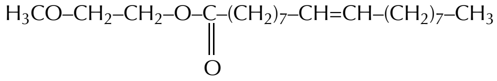
The surface compressibility coefficient (*K*) was deduced from the π-*A* isotherm curve by means of Equation 1.

$$K = -1/A_0\ (\partial A/\partial \pi) \qquad [1]$$

Molecular modeling studies with standard Alchemy computer software (IMR, Englewood, CO) have been carried out to compare the theoretical value of the minimum surface area/molecule with the experimental findings.

RESULTS AND DISCUSSION

The structural representation of 2-methoxy ethyl oleate is shown in Scheme 1. The chemical characteristics, such as acid value, iodine value and ester value, of the synthesized ester have been given in Table 1. In comparing experimental and theoretical values, the purity of the ester is estimated as 98%.



$$H_3CO{-}CH_2{-}CH_2{-}O{-}\underset{\substack{\| \\ O}}{C}{-}(CH_2)_7{-}CH{=}CH{-}(CH_2)_7{-}CH_3$$

SCHEME 1

The infrared (IR) spectrum of the ester (Fig. 1) shows characteristic peaks due to C–C_{str} vibration of CH_3 (2960, 2871 cm^{-1}), C=O_{str} vibration at 1750 cm^{-1}, –C–O–C_{str} vibration of the alcohol group at 1110 cm^{-1}. ^{1}H NMR spectral analysis (Fig. 2A) of the ester is as follows: δ 0.81 ppm (*t*, end methyl), δ 3.35 ppm (*s*, –OCH_3), δ 3.50 ppm (*t*, –OCH_2), δ 4.14 ppm (*t*, α-CH_2), δ 5.2 ppm (*t*, CH=CH). The ^{13}C NMR spectrum of the ester (Fig. 2B) is consistent with the structure of the ester and shows peaks at δ 18 ppm (–CH_3), δ 22.38 ppm $(CH_2)_n$, δ 60 ppm (–OCH_3), δ 69 ppm (–OCH_2–CH_2) , δ 130 ppm (C=C), and δ 180 ppm (C=O).

π–A *isotherm of 2-methoxy ethyl oleate.* π-*A* isotherms of 2-methoxy ethyl oleate for the selected concentrations of the ester solutions in chloroform are shown in Figure 3. The maximum surface pressure of about 26.2 mN·m^{-1} was attained at and above a concentration of 1.47×10^{-3} M (0.5 mg/mL) of the ester, which can be considered as the critical minimum concentration required for monolayer formation at the air/water interface.

The π-*A* isotherm of 2-methoxy ethyl oleate (0.5 mg/mL) at 25°C is shown in Figure 3E. The isotherm is reproducible as indicated by the exact overlap of the curves formed from three individual runs. The π-*A* isotherm of 2-methoxy ethyl ester of oleic acid performed in a quasi-static mode coincides with the normal run, thus ruling out the adsorption of solvent in the monolayer. The smooth curvature of the π-*A* isotherm suggests the absence of phase transitions of the ester at the investigated temperature. A close examination of the isotherm indicates a monotonic increase in surface pressure upon compression, indicating that the monolayer remains in the liquid expanded state.

TABLE 1
Chemical Characteristics of 2-Methoxy Ethyl Oleate

	Experimental	Calculated
Acid value[a]	2.153	0
Ester value[a]	163.9	165
Iodine value[b]	73.2	74.11

[a] mg KOH/g.
[b] g I_2/100 g.

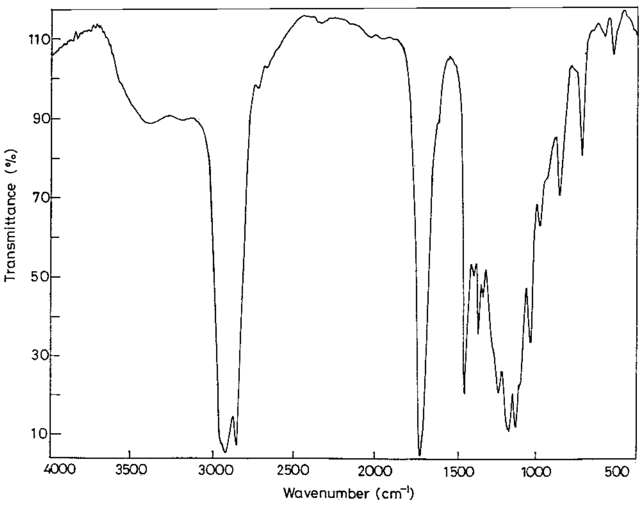


FIG. 1. Fourier transform infrared spectrum of 2-methoxy ethyl oleate in region 4000–500 cm^{-1}.

The surface characteristics were as follows: initial increase in area (A_i), 84 Å^2/molecule; collapse pressure (π_c), 25.9 mN/m; surface area per molecule at collapse pressure (A_c), 30.7 Å^2/molecule; maximum pressure (π), 26.2 mN/m; and minimum area of packing per molecule (A_0), 57.2 Å^2/molecule; of the ester film at the air/water interface at 25°C as estimated from the π-A isotherm (Fig. 3E). The limiting area, A_0 is obtained by extrapolation of the steep linear portion of the π vs. A curves to $\pi = 0$. A_c and π_c are the collapse molecular area and the collapse pressure, respectively, and they correspond to the slope change of the compression isotherms at the highest surface pressure. The initial increase in surface pressure occurs at a mean molecular area (A_i) of 84 Å^2 per molecule, in contrast to the parent acid for which A_i has been reported to be 55 Å^2 per molecule (19).

As the ester is in the liquid state at room temperature, π_c is expected to be around the equilibrium spreading pressure,

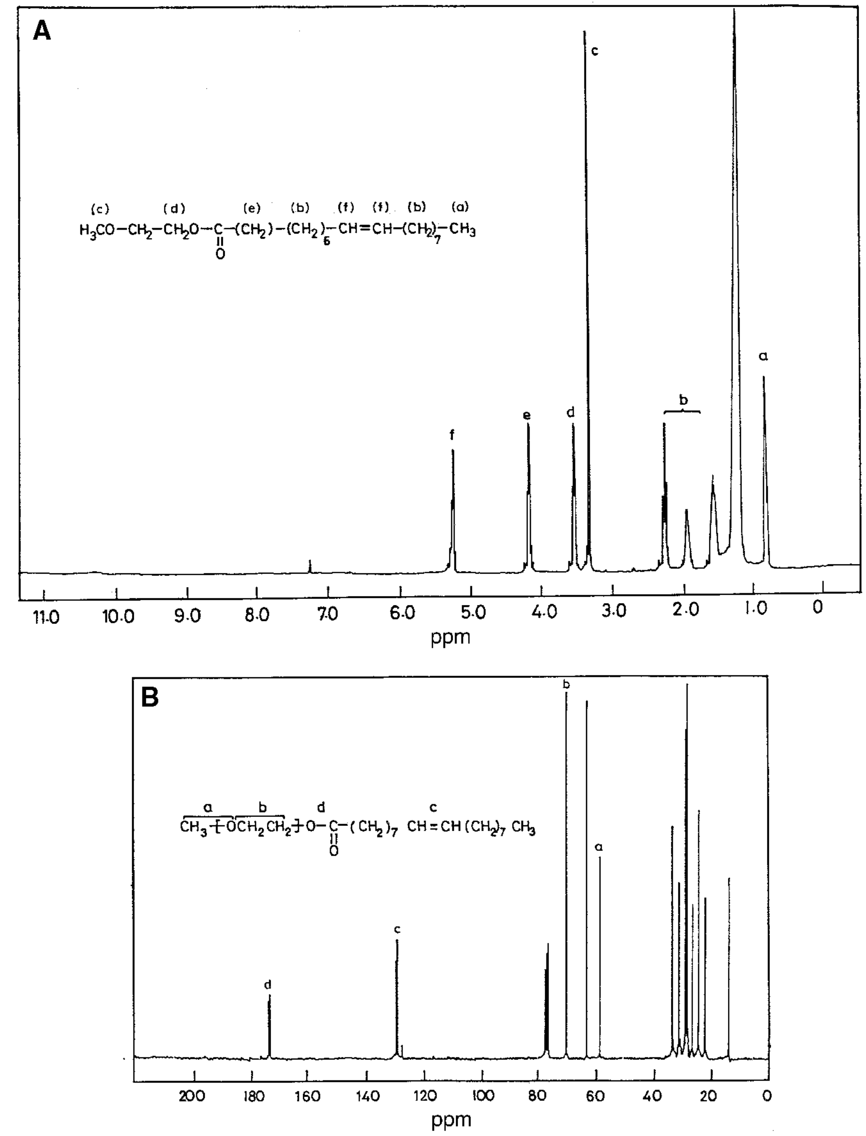


FIG. 2. (A) ^{1}H nuclear magnetic resonance (NMR) spectrum of 2-methoxy ethyl oleate in CDCl$_3$ at 300 MHz. (B) ^{13}C NMR spectrum of 2-methoxy ethyl oleate in CDCl$_3$ at 300 MHz.

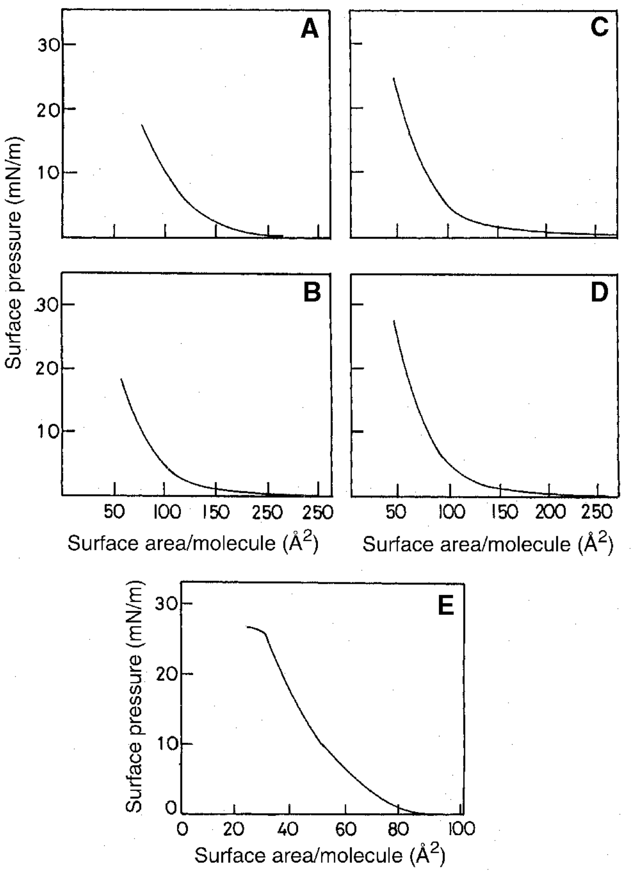


FIG. 3. Surface pressure (π)-area (*A*) isotherm at the air/water interface of 2-methoxy ethyl oleate of different concentrations at 25°C. A–E: 0.12, 0.16, 0.20, 0.24, and 0.50 mg/mL.

similar to the parent acid. Accordingly, the ester shows a collapse pressure of 26.5 mN/m at a mean molecular area of 30.73 Å^2 per molecule. The slightly lower π_c and higher A_c of the ester, in comparison to the acid (π_c = 30 mN·m^{-1}, A_c = 27 Å^2/molecule), might be arising from the hydrophilic character of the polar methoxy ethyl head group. A similar trend has been observed in respect to linoleic acid (π_c = 26 mN/m and A_c = 31Å^2/molecule) wherein the presence of a double bond in the tail portion contributes to a greater degree of polarity. It is probable that introduction of more polar sites at the head or tail group in an amphipathic system effects a decrease in the cohesive force near the polar regions with a consequent increase in contact with the water subphase.

The hysteresis cycle of the π-*A* isotherm, performed up to surface pressure of 27 mN·m^{-1}, is shown in Figure 4. Interestingly, the compression and expansion isotherms exactly overlap at π beyond the equilibrium spreading pressure, suggesting the formation of stable aggregated layers at the interface. However, this aspect is to be further confirmed by microscopic studies. The small decrease in mean surface area per molecule to the extent of about 0.02 nm^2 per molecule upon expansion throughout the entire region of the isotherm suggests dynamics of the monolayer arising from reorganization at the interface without impairing the stability of the ester film.

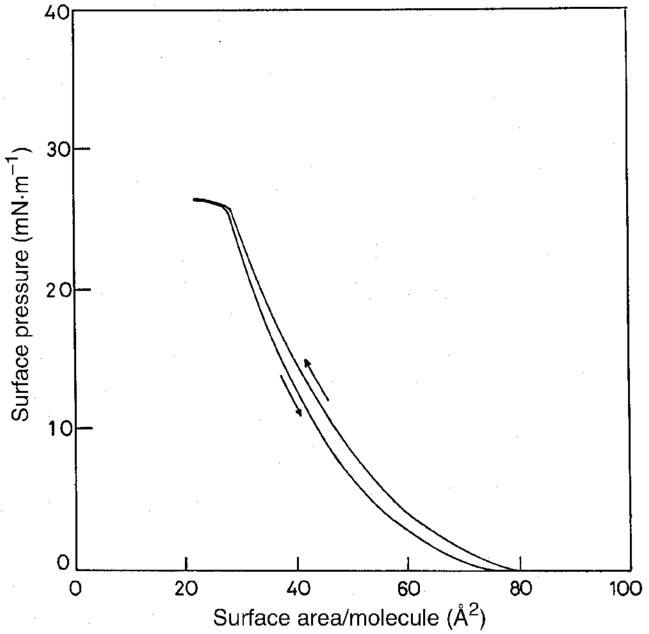


FIG. 4. Hysteresis of π-*A* isotherm of 2-methoxy ethyl oleate at the air/water interface (25°C). For abbreviations see Figure 3.

Figure 5 depicts stability of the ester monolayer at various pressures of 10 (curve 1), 15 (curve 2), and 20 (curve 3) mN·m^{-1}, which show the change in surface area per molecule with time recorded for a period of 20 min. The linear curves with single slopes, obtained at all surface pressures, indicate the occurrence of a one-step relaxation process. The relaxation rates, estimated at different pressures from the slope of the plot of change in surface area with time, and the total loss in surface area of the monolayer after a period of 20 min are shown in Table 2. At the lower surface pressures of 10 and 15 mN·m^{-1}, the ester exhibits the same relaxation rates, 0.561 s^{-1}, suggesting a typical reorganization process. However, the

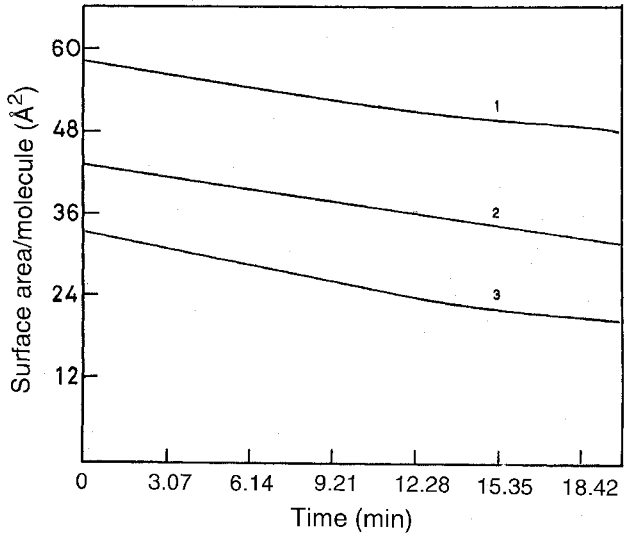


FIG. 5. Plot of change in surface area/molecule (Δ*A*) as a function of time at different surface pressure. Curves 1–3: π = 10, 15, and 20 mN·m^{-1}. For abbreviations see Figure 3.

TABLE 2
Stability and Relaxation Rates of 2-Methoxy Ethyl Oleate at the Air/Water Interface[a]

Surface pressure (π) (mN/m)	Relaxation rates (Å^2/molecule/s)	Δ*A* (%) after 20 min
10	0.59 ± 0.01	17.52
15	0.59 ± 0.01	16.04
20	0.78 ± 0.02	36.36

[a] *A*, area.

higher relaxation rate (0.781 s^{-1}), exhibited at $\pi = 20$ mN·m^{-1}, indicates a probable change in the packing behavior of the ester film.

The minimum area of packing (A_0) of the ester in the liquid expanded region at the air/water interface is estimated as 57.2 Å^2 per molecule from the π-*A* isotherm (Fig. 3E). The large increase in A_0 of the ester, when compared to the parent acid (A_0, 41 Å^2/molecule), suggests more expanded conformation of the ester. This may be arising from the flat conformation of the head group, comprised of methoxy ethyl ester. Here, the adsorption of the ester monolayer at the air/water interface is facilitated by hydrogen bond interaction between the aqueous subphase and the hydrophilic oxygen present in the head group, and the electrostatic interaction among the polar double bond can be anticipated.

The surface compressibility coefficient *(K)* has been deduced from the steep linear portion of π vs. *A* curves (Fig. 3E) and the corresponding limiting molecular area, A_0 (Eq. 1). Generally, the *K* value at different pressure regions is used to draw inference with respect to the phase transitions occurring in the monolayer system. The compressibility coefficients of the ester at different pressures, ranging from 4–24 mN·m^{-1}, were calculated and plotted as a function of pressure (Fig. 6). Taking into account the *K* values indicated for different monolayer states, namely 5×10^{-4}–10^{-3} m/mN for solid (*S*), 4×10^{-3}–10^{-2} m/mN for liquid condensed, and 2×10^{-2}–6×10^{-2} m/mN for the liquid expanded states, the actual state of the monolayer can be inferred. A close examination of the plot suggests that the compressibility coefficient increases from 0.042 to 0.057 m/mN in the pressure region of 4–12 mN/m. A sudden drop in *K* to a value of 0.0354 m/mN occurs when $\pi = 14$ mN/m, and interestingly, *K* remains in the range of 0.03 to 0.0352 m/mN in the high-pressure region of 16–22 mN·m^{-1}. The higher compressibility coefficient exhibited in the low-pressure region is understandable, and it indicates a more expanded structure of the ester film. Furthermore, the lower *K* value of the ester film at surface pressure >15 mN·m^{-1} suggests a much closer packing of molecules, tending toward formation of a liquid condensed state, intermediate between the gaseous and solid states in positional order. The negligible change in *K* in the higher pressure region suggests formation of a monolayer film with the possible maximal degree of packing in the liquid expanded state at the interface. Typically, the breakpoint in the packing behavior appears to occur at $\pi = 14$ mN/m. It is further inferred that *K* of the ester film is slightly higher than for the parent acid (ester, 0.037–0.045 m/mN, acid 0.022–0.0175 m/mN). Such higher *K* values for the ester thus suggest more expanded conformation of the ester due to introduction of the methoxy ethyl group, and this observation is in accordance with the increased A_0 of the ester film.

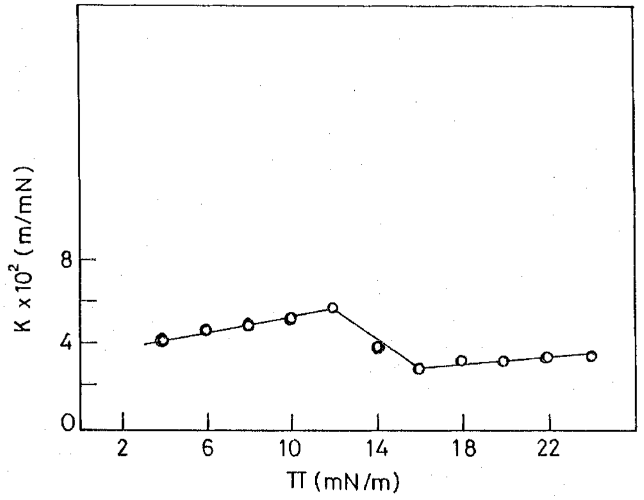


FIG. 6. Plot of compressibility coefficient (*K*) vs. surface pressure (π) of 2-methoxy ethyl oleate film at the air/water interface, 25°C.

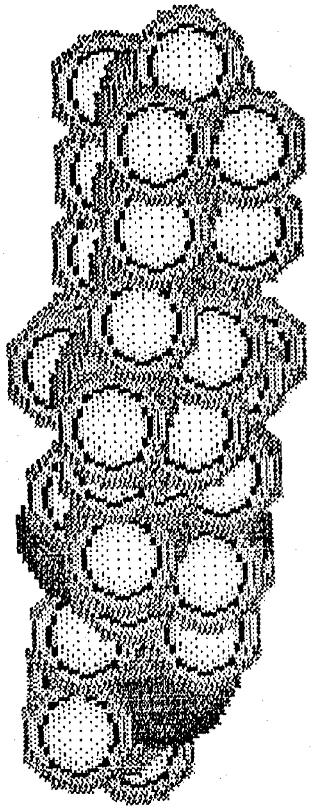


FIG. 7. Molecular model of projected 2-methoxy ethyl oleate molecule at the air/water interface (standard Alchemy software).

The minimized structure for the projected ester molecule at the air/water interface is shown in Figure 7. The area corresponding to this structure is 54.2 Å^2/molecule, and this agrees reasonably with the experimental value (57.2 Å^2) as estimated from the π–A isotherm.

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