667. *Monolayer Properties of Elaidyl Alcohol.*

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A series of compression isotherms has been obtained for elaidyl alcohol. At room temperature, the alcohol gives a liquid expanded monolayer, exhibiting a transition to the condensed state. An attempt has been made to measure the energy change involved in the transition.

The introduction of a double bond into a long-chain amphipathic molecule results in markedly more expanded films at the air–water interface (Adam, *Proc. Roy. Soc.*, 1922, *A*, **101**, 516; Marsden and Rideal, *J.*, 1938, 1163). When the unsaturated substance has the *cis*-configuration, it is clear that steric factors reduce the intermolecular cohesion of the hydrocarbon long chains. For the *trans*-configuration, however, the reason is not so obvious. Adam (*loc. cit.*) has ascribed the expansion to the hydrophilic nature of the double bond, but Marsden and Rideal (*loc. cit.*) consider this factor insufficient to account fully for the observed expansion. The latter view is also held by Schneider, Holman, and Burr (*J. Phys. Coll. Chem.*, 1949, **53**, 1016).

In connection with other work, it became necessary to obtain the force–area (π–A) curve of elaidyl alcohol (*trans*-$CH_3\cdot[CH_2]_7\cdot CH\colon CH\cdot[CH_2]_7\cdot CH_2\cdot OH$). The result obtained differed considerably from that of Marsden and Rideal, in that the isotherm was of the liquid expanded type exhibiting a transition region into the condensed form. Since elaidyl alcohol is the only *trans*-unsaturated alcohol of which the π–A curve is known, the present results were deemed worthy of record.

The surface balance was of the Langmuir–Adam type, as modified by Alexander (*Nature*, 1947, **159**, 304). Compression curves were recorded automatically by a revolving drum and pen recorder. The film was compressed at a constant rate, by a movable barrier coupled to a piston immersed in a cylinder of oil. The balance was enclosed in a box and kept at constant temperature (±0·1°) by circulating water. The rate of compression did not affect the shape of the π–A curve. Details of the automatic surface balance will be described elsewhere. Surface potential measurements were obtained with a manually operated balance, a polonium air electrode being used.

Pure elaidyl alcohol (m. p. 34°) was provided by Professor T. P. Hilditch, to whom our thanks are due. It was spread from an ethanol–benzene mixture by means of an Agla micro-syringe.

Results and Discussion.—Fig. 1 shows a series of π–A isotherms for elaidyl alcohol spread on distilled water. It was not practicable to work below 2·9°. Above 12°, the monolayer was of the liquid expanded type, exhibiting a transition into the condensed region. The present technique could not detect any temperature effect on the π–A curve of the liquid expanded region between 12·3° and 25·2°. Above 25° this region showed a slight expansion. The monolayer was fluid at all areas down to the collapse (21 A.^{2}). Further compression resulted in a marked drop in film fluidity. At temperatures below 40° the film solidified at *ca.* 16 A.^{2}; above this temperature the film remained fluid. The π–A curve was completely reversible (even past the collapse area) over the whole temperature range investigated. We note that the "critical temperature of crystallization" (Dervichian, *J. Chem. Physics*, 1939, **7**, 931) is between 27·3° and 36·4°, in which range lies the three-dimensional m. p. (34°).

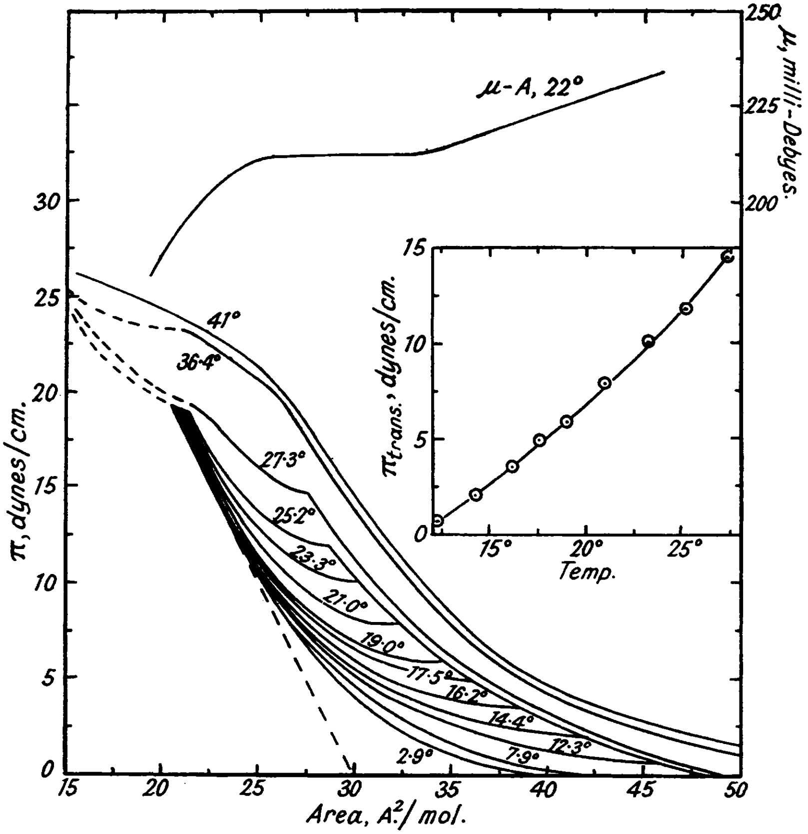
Compression of the monolayer over the liquid expanded region resulted in a gradual drop in μ, the surface moment, which then remained constant (200 milli-Debyes) over the transition region. No fluctuations greater than 6 mv. in the surface potential were observed over this region.

Marsden and Rideal have stated that elaidyl alcohol gives a condensed type of monolayer at 21°. The present work shows, however, that at this temperature, elaidyl alcohol forms a liquid expanded film (limiting area = 48 A.^{2}), with a transition into the condensed form at π = 8 dynes/cm. (32·5 A.^{2}). The m. p. of the previous workers' sample was 10° lower than that of the present sample, which had a value conforming with that in the literature. It is clear, therefore, that the difference in monolayer behaviour arises out of the impurity of the previous specimen. *trans*-Unsaturation thus has a greater expanding effect on a long-chain alcohol than has hitherto been thought. It seems that, in spite of the similarity between a *trans*-unsaturated configuration and a saturated one, this expansion is caused to an appreciable extent by difficulties in adlineation of the unsaturated chains. Stenhagen (private communication), for example, has found octadec-17-enoic and octadec-17-ynoic acid to give completely condensed monolayers, whereas if the hydrophilic nature of the unsaturated bond were responsible for expansion one would have expected these two compounds to give highly expanded films.

The series of isotherms (Fig. 1) is of the same type as first obtained by Adam and Jessop (*Proc. Roy. Soc.*, *A*, 1926, **112**, 362) for myristic acid. The half-expansion temperature ($T_{\frac{1}{2}}$) is seen to be $<10°$; this value may be compared with an estimated $T_{\frac{1}{2}} = 74°$ for the saturated C_{18} alcohol. The introduction of *trans*-unsaturation into the long-chain alcohol thus results in a fall of $>64°$ in $T_{\frac{1}{2}}$ (cf. the analogous fall for a C_{18} acid of *ca.* 46°; Adam, "The Physics and Chemistry of Surfaces," London, 1941) and is a reflection of a reduction in intermolecular cohesion caused by the double bond.

FIG. 1.

π–A and μ–A Isotherms for elaidyl alcohol, spread on distilled water. Inset: *$\pi_{trans.}$–temp. relationship.*



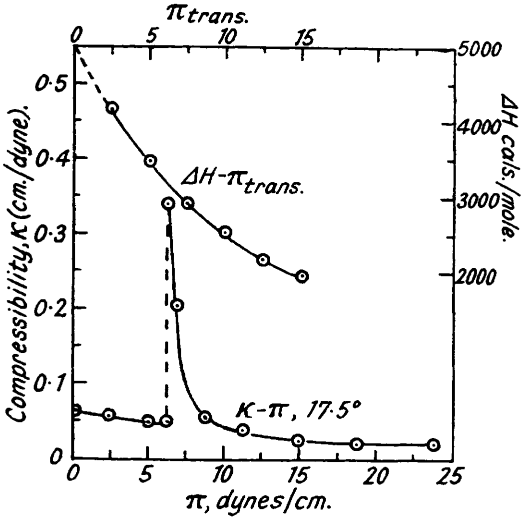
The liquid expanded region obeys Langmuir's equation (*J. Chem. Physics*, 1933, **1**, 756), *viz.*, $(\pi - \pi_0)\ (A - A)_0 = kT$, where π_0 is the negative spreading pressure of the hydrocarbon chains and A_0 is an empirical constant related to the cross-sectional area of the molecule. The following values are obtained: $A_0 = 10{\cdot}3$ A.², $\pi_0 = -10{\cdot}0$ dynes/cm. The former value is less than the value (15·76 A.²) obtained by Marsden and Rideal for the *cis*-alcohol (oleyl alcohol), a result which is undoubtedly connected with the greater cohesion allowed by the *trans*-configuration; this phenomenon is also observed with long-chain unsaturated acids (Marsden and Rideal). We note that, in general, alcohols have lower A_0 values than the corresponding acids, and that the $T_{\frac{1}{2}}$ values of alcohols are higher than those of corresponding acids, which suggests that the alcohol head group exhibits greater intermolecular cohesion than that of the acid.

The nature of the transition of a monolayer from the liquid expanded state to the condensed has been discussed by several authors (Gregg, "Surface Chemistry," Butterworth, London, 1949; Dervichian, *loc. cit.*; Harkins, Boyd, and Young, *J. Chem. Physics*, 1940, **8**, 954; Langmuir, *loc. cit.*). It is clear that the transformation is not one of "first order" (Ehrenfest, *Proc. K. Akad. Amsterdam*, 1933, **36**, 115); it is equally clear from the sudden discontinuities (*e.g.*, 36·0 A.² at 17·5°) in the π–A curves that the transformation is not one of "diffuse first order"

(Mayer and Streeter, *J. Chem. Physics*, 1939, **7**, 1017; Gregg, *loc. cit.*). The compressibility, $K = (\mathrm{d}A/\mathrm{d}\pi)/A$, is plotted as a function of the monolayer pressure in Fig. 2 (17·5°), and comparison with similar plots for transitions of different orders shows that the above transformation is intermediate between first order and diffuse first order; certainly it is not of a higher order. This being so, the possibility of obtaining a latent heat of transformation becomes of interest. The application of a two-dimensional Clausius–Clapeyron equation, $\mathrm{d}\pi_{\mathrm{trans.}}/\mathrm{d}T = \Delta H/T\Delta A$ (Glazer and Alexander, *Trans. Faraday Soc.*, in the press), where $\pi_{\mathrm{trans.}}$ is the transition pressure, ΔA is the difference in molar area of the two phases, and ΔH is the latent heat of transformation, is not strictly valid since the pressure is not constant over the transition region. We feel, nevertheless, that some indication of the magnitude of the latent heat can be obtained by such an application. It would seem from the compressibility diagram (lower curve, Fig. 2) that the departure from first-order behaviour is probably not as serious as appears from the variation of the pressure over the transition region. This increase in pressure corresponds to an increase in the surface Gibbs free energy ($\Delta G = \int A\,.\,\mathrm{d}\pi$). Calculation shows that this free-energy increase is only *ca.* 100 cals./mole.

FIG. 2.

Lower curve : *Compressibility–pressure diagram at* 17·5° *for the transition liquid expanded to condensed.* Upper curve : *Relationship between* ΔH *and* $\pi_{trans.}$ *for the transition.*



The ΔH values have been obtained by considering the condensed form of the monolayer to be linear and having a limiting area of 30 A.^{2} (broken line in Fig. 1). Although it was not possible to reduce the temperature sufficiently to obtain the completely condensed form, the general tendency is clear from the figure. A plot of $\pi_{\mathrm{trans.}}$ (pressure at the kink point) against temperature is shown in Fig. 1 (inset); ΔH values were obtained by measuring the slope $\mathrm{d}\pi_{\mathrm{trans.}}/\mathrm{d}T$ along the curve. Fig. 2 (upper curve) shows a plot of ΔH against $\pi_{\mathrm{trans.}}$. Since $\Delta H = \Delta E + \pi\,.\,\Delta A$ (ΔE is the change in internal energy for the transition), extrapolation to zero pressure gives $\Delta E = 5000$ cals./mole. Application of the Langmuir equation, $\log(\pi_{\mathrm{trans.}} - \pi_0) = C - B_n/T$, leads to a value 9700 cals./mole for the "latent heat of micelle formation." A knowledge of the extent to which the double bond contributes to ΔE must await a similar study of the compression isotherms of the corresponding saturated alcohol.

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