710. *The Properties of Freshly Formed Surfaces. Part XIII. The Compressibility of Soluble Films of Decyl and Other Alcohols.*

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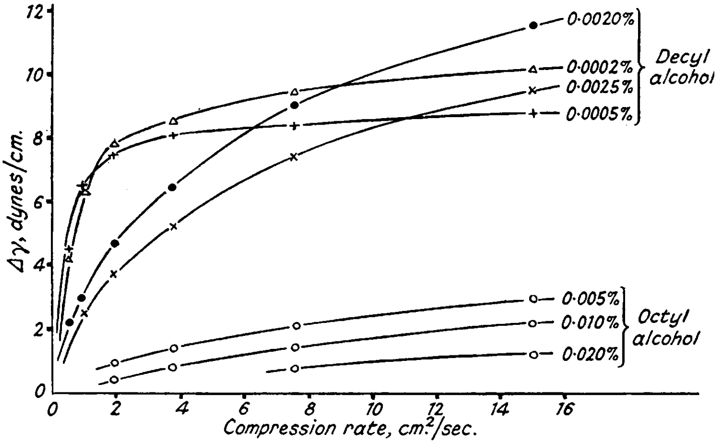
The influence of compression rate on the compressibility of soluble films of decyl (and lower) alcohols has been studied by using the vertical-plate method together with a trough and rapidly moving barrier. Both equilibrium and non-equilibrium surfaces have been studied in order to assess the relative significance of surface excess and bulk concentration. Desorption from a compressed monolayer has been found to be almost instantaneous.

The pouring of a decyl alcohol solution from its containing vessel into a trough is equivalent to compression of the surface (Part XII, preceding paper), but under given experimental conditions the rate of compression cannot be varied. The present paper is concerned with the influence of compression rates on the properties of equilibrium and non-equilibrium surface films.

Surface tensions were measured by the vertical-plate method. The solution was contained in a small rectangular waxed trough having internal length 10·0 cm. and width 6·43 cm. In each experiment a waxed barrier was placed on the trough parallel to the shorter edge and in such a position that the surface area surrounding the vertical plate, before compression, was 61·2 cm.^{2}. The surface was then compressed by moving the barrier, at constant speed, through a distance of 3·5 cm. to reduce the area to 38·7 cm.^{2}. In all experiments these initial and final areas were standard.

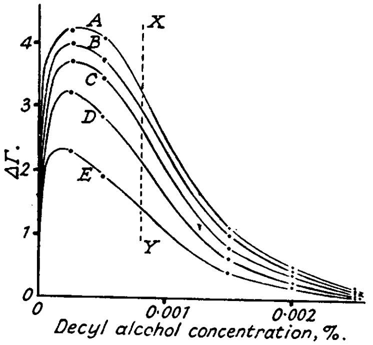
Fig. 1.



Compression of Equilibrium Surfaces.—Before each determination the surface of the solution was swept, the barrier placed in its initial position, and the surface allowed to recover its equilibrium tension. The surface was then compressed, and the results obtained at 22° with solutions of *n*-decyl and *n*-octyl alcohols are given in Fig. 1. The tension fell during the compression process; the decrease in tension is, of course, a function of the extent of compression and the $\Delta\gamma$ values in Fig. 1 represent the full decrease brought about by compression from 61·2 to 38·7 cm.^{2}. Each point in Fig. 1 therefore represents a separate experiment. The highest compression rates shown are obtained by movement of the barrier through 3·5 cm. in 1·5 secs. Various mechanical devices for moving the barrier smoothly and rapidly were considered, but it was found most convenient, and the results were quite reproducible, when the barrier was moved by hand and a half-second metronome employed. It would appear from the decyl alcohol results in Fig. 1 that, although there is a general increase in $\Delta\gamma$ with rate of compression, it is difficult to correlate this increase in tension with concentration. However, the compressibility of a soluble film may be defined as the extent to which the equilibrium surface excess may be exceeded as a result of reduction in area. Accordingly, for any given concentration, the $\Delta\Gamma$ values equivalent to $\Delta\gamma$ may be accepted as a measure of the compressibility of the film. The decyl alcohol results in Fig. 1 have therefore been transcribed into $\Delta\Gamma$–concentration curves in Fig. 2, and the system so obtained is quite regular.

Over the range of concentrations and compression rates given in Fig. 2, it was observed that in no case did compression of the surface lower the surface tension appreciably below the monolayer value (32·5 dynes/cm.). At concentrations below that shown by the line *XY* (Fig. 2) the standard area reduction was not sufficient to produce a monolayer at the smaller surface area. Over the major range of concentration, *i.e.* above *XY*, a monolayer is produced, and it follows from Fig. 2 that desorption from the compressed monolayer must be almost instantaneous. Considering concentration *XY*, the standard compression would increase the surface excess (in the absence of desorption) from the equilibrium value ($7·7 \times 10^{-8}$ g./cm.^{2}) to the monolayer ($12·2 \times 10^{-8}$ g./cm.^{2}). Fig. 2 (Curve *A*) shows that the $\Delta\Gamma$ value obtained is $3·2 \times 10^{-8}$ g./cm.^{2}, so that an amount $1·3 \times 10^{-8}$ g./cm.^{2} is desorbed from the film in the 3-second compression interval. At higher concentrations the monolayer is reached at an earlier stage in the compression process. For instance, at a concentration of 0·002%, Γ equilibrium $= 11·6 \times 10^{-8}$ g./cm.^{2}; the standard compression, in the absence of desorption, would increase this to $18·3 \times 10^{-8}$ g./cm.^{2}, whereas experiment shows that the increase in surface excess which actually occurs, for a 3-second compression interval, is only $0·6 \times 10^{-8}$ g./cm.^{2}, which is the difference between Γ equilibrium and Γ monolayer. It follows that compression of the monolayer has resulted in the desorption of $6·1 \times 10^{-8}$ g./cm.^{2}, a value considerably in excess of that obtained when no monolayer compression occurs. This result is in accord with the general principles already outlined; desorption from an uncompressed monolayer is hindered by the energy barrier, but compression of the monolayer involves the transfer of additional energy to the surface molecules, so that desorption from a compressed monolayer is virtually an unhindered process. As the concentration is decreased below *XY*, the compressibility is maintained at a high value until Γ, and consequently $\Delta\Gamma$, ultimately falls to zero. It is noteworthy that the slower the compression rate (Fig. 2), the greater is the time available for desorption, and this is reflected in a lower compressibility.

Fig. 2.



Curve.	Time of compression from 61·2 *to* 38·7 *cm.*^{2} (*seconds*).
A	3
B	6
C	12
D	24
E	48

It will be seen from Fig. 1 that the compressibility of *n*-octyl alcohol is considerably less than that of decyl alcohol. Identical experiments have been carried out on *n*-heptyl alcohol, the compressibility being very slight, and on *n*-hexyl alcohol, the compressibility being scarcely detectable. These experiments therefore confirm the results described in Part XII (previous paper).

Compression of Non-equilibrium Surfaces.—In the above experiments a range of Γ values has been obtained by using solutions of different concentrations, but the results indicate that the compressibility of the film may be interpreted in terms of the surface excess rather than of the number of solute molecules in the bulk solution. The relatively slow rate of desorption of decyl alcohol into its solutions provides a unique opportunity for investigating this aspect further. When the surface is given an excess of alcohol beyond the equilibrium value (*e.g.*, by the pouring process) about 500 seconds are required, at 20°, before equilibrium is restored. Thus a range of Γ values is available for a single concentration, and a number of compressibility measurements may be made during the desorption process. The experimental results are shown in Fig. 3. For each concentration the solution was poured into the trough under standard conditions and the fall in tension which occurred when the barrier was moved between its standard limits, in a 3-second time interval, was measured immediately. The experiment was repeated several times, different measured time intervals being allowed to elapse between the pouring of the solution and the measurement of compressibility. The compressibility values, expressed as $\Delta\Gamma$

and deduced from the data in Fig. **3**, are plotted in Fig. 4 against the excess on the the surface immediately before the measurement of compressibility, together with the corresponding values obtained under the same experimental conditions for equilibrium surfaces. The results for all concentrations lie close to a single smooth curve. These results therefore provide independent support for the conclusion reached on the basis of the spreading experiments (Part XII, preceding paper), *viz.*, that desorption rates in systems of this type are primarily a function of surface excess rather than of bulk concentration.

FIG. 3.

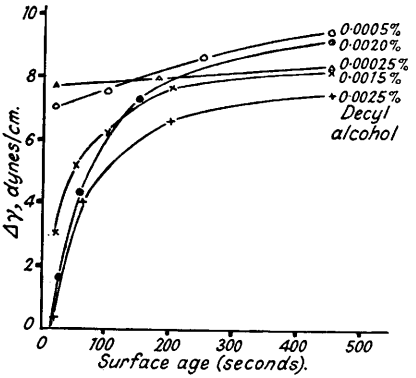
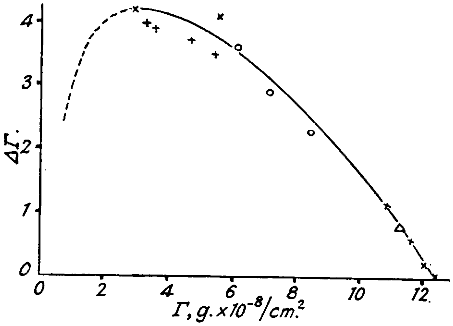


FIG. 4.



Equilibrium surfaces, ×.
Non-equilibrium surfaces :
+ 0·00025% *decyl alcohol.*
○ 0·0005% ,,
△ 0·0015% ,,

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