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In the present work measurements on the surface viscosity of monomolecular films of n-long chain alcohols (C_{16} to C_{22}), corresponding alkoxy ethanols and their mixtures were carried out especially to get informations about the nature of two dimensional phase transformations, free energy of activation for viscous flow (ΔF), relaxation time (τ) and intermolecular interaction \( \tilde{w}_{1-k}(0.94 r_1) \) and to provide basic data to elucidate the permeability of water through their monolayers formed on water surface.

The surface viscosity of n-long chain alcohols and alkoxy ethanols was studied at four different temperatures (15°C-30°C) as a function of pressure (2-40 dynes/cm.) and of shear rates (0.12-1.8 sec.\(^{-1}\)). The mixed monolayers of the alcohols and alkoxy ethanols in 1:0.5, 1:1 and 1:2 molar proportions were studied at one temperature only. The transition pressures obtained from the \( \mu-\Pi \) isotherms were compared with those of the \( \Pi-A \) isotherms. For comparing the transition pressures of mixed films the \( \Pi-A \) measurements were also carried out independently at the same temperature as used in the \( \mu-\Pi \) measurements. For calculating \( \Delta F \), the area/molecule obtained actually from \( \Pi-A \) isotherms were used instead of taking the hitherto practiced standard values.
From the results, the following observations were noted:

**Alcohols**

Studies of the effect of temperature on surface viscosity have revealed many unusual behaviour of the films of n-long chain alcohols. The surface viscosity of \( \text{C}_{16}-\text{OH} \) and \( \text{C}_{18}-\text{OH} \) increases with temperature whereas in the case of \( \text{C}_{20}-\text{OH} \) and \( \text{C}_{22}-\text{OH} \) it decreases. The L3 phase was obtained by a first order or second order change depending on the nature of the film and temperature.

The surface viscosity increases abruptly at transition point showing a sharp break in the \( \mu-\Pi \) curves. This has been attributed to the \( \text{L}_c \rightarrow \text{I} \) transition rather than designating the same as the \( \text{L}_c \rightarrow \text{S} \) transition done during the earlier \( \Pi-A \) isotherm studies. The transformations are more pronounced in \( \mu-\Pi \) measurements than in \( \Pi-A \) isotherms.

The \( \text{L}_c \rightarrow \text{I} \) transition region becomes wider as the temperature is increased.

The transition pressures \( \text{L}_c \rightarrow \text{I} \) or \( \text{L}_c \rightarrow \text{L3} \) obtained from \( \mu-\Pi \) curves at different temperatures agree well with that indicated by \( \Pi-A \) isotherms.

The surface viscosity decreases with increase in shear rate.
The $\mu$ of the L3 phase does not decrease much at higher temperatures especially at higher shear rates.

The decrease in the viscosity in the L3 phase may be due to strong hydrogen bonding between film molecules and weaker interaction with the water molecules in the subphase.

The free energy of activation ($\Delta F$), residual free energy ($\Delta F'$), relation time ($\tau$) and intermolecular interaction for molecular spacing $0.94 r_1$, $\psi_{1-k}(0.94 r_1)$, were calculated from the $\mu_0$ and $\mu_\infty$ ($\mu_0$ = surface viscosity at zero shear rate and $\mu_\infty$ = surface viscosity at infinite shear rate) values at the $L_\text{c} \rightarrow I$ or $L_\text{c} \rightarrow L_3$ transition, obtained by extrapolating the $\mu$ vs $g$ curve. $\mu_0$ and $\mu_\infty$ values for C$_{16}$-OH and C$_{18}$-OH increase with increase in temperature except at 30°C for C$_{16}$-OH while it decreases in the case of C$_{20}$-OH and C$_{22}$-OH. $\tau$ increases with increase in chain length but for C$_{22}$-OH between 20°C and 30°C. The interaction energy increases with increase in temperature for all alcohols studied.

Alkoxy Ethanol

Many of the peculiarities observed in the case of alcohols with temperature variation are also observed in the case of alkoxy ethanols. The surface viscosity of C$_{16}$-OC$_2$H$_4$OH and C$_{18}$-OC$_2$H$_4$OH increases with increase in temperature but in the case of C$_{22}$-OC$_2$H$_4$OH it decreases.
C_{18}^{}-OC_{2}^{}H_{4}^{}OH exhibited a very low viscosity at 15°C and 20°C. In the case of alkoxy ethanols the LS phase exists for a particular temperature and for a particular film and was obtained by a second order change depending on compound and temperature.

In case of alkoxy ethanols also (i) the surface viscosity abruptly increases in the transition region showing a sharp break in \( \mu-W \) curves. Here also the transitions are more pronounced in the \( \mu-W \) curves than in the \( \Pi-A \) isotherms, (ii) the transition pressures obtained agree well with those indicated by \( \Pi-A \) isotherms, (iii) the \( L_{C} \rightarrow I \) region becomes broader as the temperature increases, (iv) the surface viscosity decreases with the increase in shear rate. The decrease in the LS phase at higher shear rate is much less compared to that at lower shear rates.

For alkoxy ethanols \( \Delta F, \Delta F', \tau \) values have calculated from \( \mu_{0} \) and \( \mu_{\infty} \) values. \( \mu_{0} \) and \( \mu_{\infty} \) values increase for \( C_{16}^{}-OC_{2}^{}H_{4}^{}OH \) and \( C_{18}^{}-OC_{2}^{}H_{4}^{}OH \), but decrease for \( C_{22}^{}-OC_{2}^{}H_{4}^{}CH \). The relaxation time \( \tau \) increases as the temperature is increased in the case of \( C_{16}^{}-OC_{2}^{}H_{4}^{}OH \) and \( C_{22}^{}-OC_{2}^{}H_{4}^{}OH \).

**Mixed Films**

The mixtures were studied at 25°C except the \( C_{20}^{}-OH + C_{20}^{}-OC_{2}^{}H_{4}^{}OH \) at 15°C. The LS phase which was
observed for alcohols and alkoxy ethanols is observed in the case of mixed films also. Here also the L3 phase obtained depends upon the nature of the mixed film. (1) The transition pressures obtained in $\mu$-$\Pi$ curves agree well with that indicated in the $\Pi$-$A$ isotherms and breaks at the transition points are sharper in the $\mu$-$\Pi$ curves than in the $\Pi$-$A$ isotherms. (ii) The surface viscosity decreases with increase in shear rate. (iii) The decrease in surface viscosity after the $L_c \rightarrow I$ transition is reduced as the shear rate is increased.

The $\Delta F$, $\Delta F'$, $T$ and $w_i-k(0.94 \, r_i)$ values were calculated using $\mu_0$ and $\mu_\infty$. The $\mu_0$ and $\mu_\infty$ values gradually increase as the composition of $C_{18}$-OH + $C_{18}$-CC$_2$H$_4$OH and $C_{20}$-OH + $C_{20}$-CC$_2$H$_4$OH is changed from 1:0.5 to 1:2.7 molar proportions but in the case of $C_{16}$-OH + $C_{16}$-CC$_2$H$_4$OH mixed films the $\mu_0$ and $\mu_\infty$ values slightly decrease at 1:1 molar proportion and then again increase at 1:2 molar proportion. $T$ values did not show any systematic variation with the composition of the different mixed films studied.

The various $\mu$ values obtained for alcohols, alkoxy ethanols and their mixed films as a function of pressure and temperature were explained on the basis of three intermolecular interactions i.e. (i) van der Waal's attractive forces between hydrocarbon chains, (ii) hydrogen bonding interaction, and (iii) dipole-dipole repulsive forces between polar groups.