JUN 9 1963

IS-574

Propagation Characteristics of Capillary Ripples, III.

Capillary Ripple Velocity and Attenuation Dispersion on Clean Water
Surfaces and on Various Monolayers*

J. Adin Mann, Jr.** and R. S. Hansen

Institute for Atomic Research and Department of Chemistry

Iowa State University, Ames, Iowa

MASTER

ABSTRACT

The theory and instrumentation previously described by us were applied to the systems monolayer-free distilled water; stearic acid, mixed hexadecanol and octadecanol, and several long chain fatty ester monolayers; stearic acid - polyvinyl acetate mixed films and egg albumen spread films; heptanoic acid adsorbed monolayers.

Experimentally determined velocities of propagation and amplitude attenuations agreed with theory to within 1% and 7% respectively with distilled water and the insoluble monolayers (using limiting formulae for highly viscoelastic films). Data for heptanoic acid soluble films were considerably less reproducible, with frequency dependence of velocity of propagation appearing to deviate somewhat from theoretical expectation.

* Contribution No. 1250. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Based in part upon a dissertation submitted by J. Adin Mann, Jr. to the Graduate College, Iowa State University, Ames, Iowa, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1962.

** Present address: van't Hoff Laboratory, University of Utrecht, Utrecht, The Netherlands. Permanent address after September, 1963: Department of Chemistry, University of Hawaii, Honolulu 14, Hawaii.

This paper was submitted for publication in the open literature at least 6 months prior to the issuance date of this Microcard. Since the U.S.A.E.C. has no evidence that it has been published, the paper is being distributed in Microcard form as a preprint.

Facsimile Price \$ 2.60

Microfilm Price \$ 86

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

INTRODUCTION

While the theory of capillary ripple propagation has received the attention of a number of workers, the experimental techniques for measuring the propagation parameters had not advanced beyond the stage set by Brown (1) in 1936 prior to the present research. In a previous paper (2), we have described a new approach to the measurement of capillary ripple characteristics. This paper will report results of measurements made with this instrumentation on representative surface film types and will compare these results with predictions of our theory presented earlier (3).

EXPERIMENTAL

Compression-expansion isotherms, dependence of capillary ripple wave length on frequency at different spreading pressures, and dependence of capillary ripple damping on frequency at different spreading pressures were determined for each system studied. A Langmuir-type all-teflon automatic recording surface balance was designed and built for the measurement of compression-expansion isotherms and for the monitoring of film spreading pressure during ripple experiments (4). The ripple damping and wave lengths were calculated from the observed phase and amplitude attenuation of a vibrating blade positioned on the film surface and responding to plane standing waves formed by a thin rod (generator) placed on the surface and forced into vertical sinusoidal motion (2). This section will discuss experimental aspects not covered in our preceding papers (2, 3, 4).

Film Spreading

The insoluble films were spread from solution using well-documented techniques, see for example discussions by Adam (5), Harkins (6),

Adamson (7), and Davies and Rideal (8). Solvent retention by the monolayer was minimized by use of low boiling (36°C) petroleum ether as spreading solvent. Benzene was generally much less satisfactory; apparently from 4 to 12 hours were required for the solvent to evaporate sufficiently for reproducible compression-expansion isotherms and ripple propagation characteristics to be obtained. This problem has been discussed extensively by La Mer (9).

Incomplete spreading problems were encountered with egg albumen films. Various techniques for spreading protein films have been discussed by Bull (10) and Trurnit (11); we found films spread from a single crystal to give most reproducible compression characteristics, and therefore used this technique in the present work. The co-area of $0.9 \text{ m}^2/\text{mg}$ on distilled water at pH 6 compared fairly well with literature co-area quotations of $0.9 \text{ m}^2/\text{mg}$ (Bull) and $1.1 \text{ m}^2/\text{mg}$ (Trurnit).

Surface tensions of heptanoic acid solutions were measured to 0.1 dyne/cm using a Cenco-Du Nouy tensiometer, and corrected by the formula of Zuidema and Waters (12) to give solution surface tensions to 0.2 dyne/cm.

Materials

All of the insoluble film-forming compounds had been recrystallized several times from various solvents, and had very sharp melting points checking literature values to within 0.5°C. The stearic acid sample had been prepared by Armour & Co., and the heptanoic acid, hexadecanol, and octadecanol were Eastman White Label chemicals. The egg albumen was Nutritional Biochemicals Corp. 5X recrystallized. The esters and polyvinyl acetate were research samples supplied by Proctor & Gamble & Co. and Interchemical Corp. and were used as received.

The spreading solvents, petroleum ether and benzene, were distilled through an Oldershaw 30 plate distillation column and the middle fractions, boiling at 36°C and 80°C respectively, were retained for use. Solvent alone was spread on the previously cleaned (Teflon parts were immersed in hot $\text{H}_2\text{SO}_4 + \text{HNO}_3$ for several hours followed by distilled water rinses; platinum parts were flamed) and filled film balance trough to check for possible contamination. These experiments indicated that solvent impurities could contribute an error not exceeding 0.05% of the observed spreading pressure.

Laboratory deionized-distilled water was passed through an activated carbon black adsorption column and then into an all fused silica continuous double distillation column obtained from Engelhard Industries, Inc. The surface tension of the still output agreed within experimental error with literature values (13) and was sufficiently pure for the purposes of this study; an experiment could last for approximately 8 hours before appreciable contamination became evident.

Procedure

Measurement of film properties involved the following steps:

- i. The probe separation circuit zero was found by the variable probe separation technique (2) on the monolayer-free distilled water surface.
- ii. The monolayer was spread (usually from petroleum ether) and the compression-expansion isotherm determined repeatedly with intervening time intervals until the isotherms became reproducible. The last isotherms checked published isotherms within experimental error.
- iii. The propagation velocity was determined as a function of frequency by the constant probe separation, variable frequency technique (2).

We were generally able to work in the probe separation region in which the log of receiving probe amplitude varied linearly with probe separation permitting relatively simple calculation of damping coefficient and its frequency dependence (2).

In the case of heptanoic acid (soluble) films part ii was replaced by the following: heptanoic acid solutions (two different concentrations were used) were prepared in sufficient quantity to fill the trough, and the surface tension was monitored by the ring method.

All measurements reported here were performed inside a thermostated enclosure saturated with respect to water vapor with temperature controlled within $\pm 0.05^\circ\text{C}$ at 25°C . Heptanoic acid solutions were allowed to equilibrate inside the enclosure until surface tension remained constant.

RESULTS

Results were obtained in the form of velocity of propagation as function of frequency and damping coefficient as function of frequency at various spreading pressures. Tabular data may be obtained from one of us (R. S. H.) on request. These data were converted to the dimensionless groups $y_1 = \frac{\rho\omega}{\gamma k^3}$, $y_2 = \frac{\alpha}{k}$, where ρ = bulk density, $\omega = 2\pi\nu$ where ν = frequency in cps, γ = surface tension, $k = \frac{2\pi}{\lambda}$ where λ = wave length, α = damping coefficient for comparison with the theory presented earlier (3). Figures 1 - 5 illustrate the dependence of the dimensionless groups y_1 and y_2 on frequency for distilled water, stearic acid monolayers at two spreading pressures, hexadecanol - octadecanol mixed monolayers at two spreading pressures, stearic acid - polyvinyl acetate mixed monolayers at three spreading pressures, egg albumen at one spreading pressure,

propylene glycol monostearate and 1, 3 - dipalmitoyl glyceryl phosphoric acid monolayers at three and two spreading pressures respectively, and heptanoic acid (soluble) monolayers at two spreading pressures. Tabular experimental data are available from one of us (R. S. H.) on request.

In Figs. 1 - 5, points indicate experimental data, and curves were calculated from the theory presented earlier (3) in the following manner:

i. Curves for distilled water were calculated from the first order theory for non-viscoelastic films, namely

$$y_1 = 1 - \frac{2\sqrt{2}}{3} \left(\frac{\omega \mu^3}{\rho \gamma^2} \right)^{1/2} \quad (1)$$

$$y_2 = \frac{4}{3} \left(\frac{\omega \mu^3}{\rho \gamma^2} \right)^{1/3} \left[1 - \frac{\sqrt{2}}{2} \left(\frac{\omega \mu^3}{\rho \gamma^2} \right)^{1/6} \right] \quad (2)$$

$$\alpha = \frac{4}{3} \frac{\mu \omega}{\gamma} \left[1 - \frac{\sqrt{2}}{2} \left(\frac{\omega \mu^3}{\rho \gamma^2} \right)^{1/6} \right] \quad (3)$$

These equations follow from Eqs. (33), (34a) and (35) of Reference 3 on substitution for $u_1 = \frac{\mu \omega}{\gamma k}$ of its zeroth order equivalent $u_1 = \left(\frac{\omega \mu^3}{\gamma^2} \right)^{1/3}$ in these equations; this is consistent with the order of approximation in Eqs. (1 - 3). In Eqs. (1 - 3), μ is the coefficient of viscosity and the other quantities have been previously identified.

ii. Curves for the insoluble monolayers, and also for the heptanoic acid soluble monolayers, were calculated according to the second order theory for highly (i. e. in principle, infinitely) viscoelastic

films using Eqs. (4 - 5).

$$y_1 = 1 - \frac{\sqrt{2}}{2} \left(\frac{\omega \mu^3}{\rho \gamma^2} \right)^{1/6} + \frac{1}{3} \left(\frac{\omega \mu^3}{\rho \gamma^2} \right)^{1/3} \quad (4)$$

$$y_2 = \frac{\sqrt{2}}{6} \left(\frac{\omega \mu^3}{\rho \gamma^2} \right)^{1/6} + \frac{5}{18} \left(\frac{\omega \mu^3}{\rho \gamma^2} \right)^{1/3} \quad (5)$$

These equations follow from Eqs. (41) and (42) of Reference 3 on substitution for $u_1^{1/2}$ of its first order equivalent (for highly viscoelastic films only) $u_1^{1/2} = \left(\frac{\omega \mu^3}{\rho \gamma^2} \right)^{1/6} \left[1 - \frac{\sqrt{2}}{12} \left(\frac{\omega \mu^3}{\rho \gamma^2} \right)^{1/6} \right]$; this is consistent with the order of approximation of Eqs. (4 - 5).

DISCUSSION

Figure 1 presents the dependence of y_1 and y_2 on frequency for clean water surfaces. In the case of y_1 , maximum deviation from theory is less than 5% with a mean deviation of about 2%; these correspond to deviations from theoretical velocity of propagation of less than 1.7% maximum and 0.7% mean. There is no systematic difference between results obtained by constant L and variable L techniques although the results obtained by the former technique evidently show considerably less scatter. There appears to be a small systematic deviation between data and theory; observed values of y_1 are on the average about 2% high. In the case of y_2 data show a mean scatter of about 7% about the theoretical curve, and there is no systematic deviation of results from theory. Damping coefficients obtained from small probe separation data (log amplitude not linear with probe separation) agreed well with those obtained from large probe separation data (log amplitude linear with probe separation). The only extensive damping coefficient data appearing in the literature are due to Goodrich (14) for the frequency region extending

from 30 cps to 250 cps; these data, collected by a different method, also fall on the theoretical curve.

Results obtained with clean water surfaces generally substantiate the standing wave treatment of our experimental data; deviation of results from theory is of the order of experimental error despite the fact that, in the case of the velocity of propagation, the deviation appears to be systematic. It also appears that our technique is more suitable for higher frequency (above 200 cps) ranges than that of Brown and Goodrich, although, over the frequency range studied by him, Goodrich's data show less scatter than ours.

Figures 2 - 4 compare data obtained with stearic acid, egg albumen, propylene glycol monostearate, 1,3-dipalmitoyl glyceryl phosphoric acid, 1:1 octadecanol-hexadecanol, and stearic acid-polyvinyl acetate monolayers with theoretical curves for highly viscoelastic monolayers. Experimental values of γ_1 are generally about 3% higher than theory at 200 cps, agree quite well with theory at 1000 cps, and are from 1% to 2% below theory at 1500 cps. They are in all cases significantly less than 1 (Kelvin Equation) at all frequencies as expected theoretically. Velocities of propagation are therefore given by theory to within 1% for all of these systems over the entire frequency range studied. Except for the 1,3-dipalmitoyl glyceryl phosphoric acid monolayer, experimental values of γ_2 (reduced amplitude attenuation) agreed with theory within experimental error, showing isolated deviations as great as 10% but generally agreeing with theory to within 7%. Amplitude attenuations for 1,3-dipalmitoyl glyceryl phosphoric acid monolayers were in accord with theory for the infinitely viscoelastic monolayer model at frequencies above 300 cps, but were significantly lower below 900 cps. We were unable to obtain reproducible force-area

curves for this substance on spreading either from benzene or petroleum ether solutions, and it is possible that the anomalous amplitude attenuation behavior may reflect a poorly spread monolayer.

Compression properties of stearic acid monolayers are well documented (5, 6); it is known that condensed monolayers are formed at all appreciable spreading pressures (islands at very low spreading pressures) and that the compressibility is of the order 10^{-2} dyne cm. Since the elastic constant k_e is thought to be correlated with the inverse of the compressibility we expect k_e to be about 100, u_2 to be at least as large as k_e/γ or at least 1.5. The difference in propagation characteristics for a film of this viscoelastic parameter and an infinitely viscoelastic film lies well within our experimental error.

While it is rather soluble in water compared to stearic acid, egg albumen can be spread as a very thin film with compression properties similar to conventional insoluble monolayers (10, 11). It was therefore investigated as representative of a class of naturally occurring polymers forming spread films, and we speculated that extensive chain interaction might lead to anomalous velocity dispersion correlating with non-Newtonian stress relaxation analogous to that found in bulk polymer systems. No evidence of such dispersion was found, and the dependence of velocity of propagation and amplitude attenuation on frequency were substantially identical to those for stearic acid monolayers.

Propylene glycol monostearate and 1, 3-dipalmitoyl glyceryl phosphoric acid were selected for investigation because their relatively large hydrophilic groups were expected to lead to relatively large compressibilities (and so relatively small values of k_e). The compressibility of propylene glycol monostearate in the range of spreading pressures investigated was

approximately 0.1 cm/dyne, k_e therefore is expected to be about 10, and u_2 at least k_e/γ or at least 0.15. If this were indeed the value of experiments here performed should have clearly distinguished from an infinitely viscoelastic film. Since the observed behavior was in accord with theory for an infinitely viscoelastic monolayer we conclude that u_2 for this system must be at least 1, and that either k_e is much larger than the inverse of the compressibility or that the viscous parameter k_v is sufficiently large that ωk_v is large compared to k_e over the frequency range studied. This also applies to egg albumen monolayers and probably to 1,3-dipalmitoyl glyceryl phosphoric acid monolayers (reproducible compressibility data could not be obtained for the latter substance).

A 1:1 octadecanol-hexadecanol mixed monolayer is known to undergo a two dimensional phase change (6) at a surface pressure between 16 and 18 dynes/cm at 25°C (16.4 dynes/cm according to our observation) so that the film compressibility becomes very large at this surface pressure. Dependence of velocity of propagation on frequency in this system was studied at 0.5, 9.5, 16.4, and 25 dynes/cm surface pressures, and in all cases data were represented by theory for the infinitely viscoelastic monolayer (only results at 0.5 and 16.4 dynes/cm spreading pressures are shown in Fig. 4). At its two phase equilibrium spreading pressure of 16.4 dynes/cm the film behaved as if its compressibility were very low, probably indicating that the frequencies used in this work were sufficiently great that each phase expanded and contracted independently without change in local relative amounts during ripple propagation.

Ries and Walker (15) have recently studied force-area characteristics of stearic acid-polyvinyl acetate mixed monolayers. It appears

that at low pressures stearic acid and polymer molecules share the surface, but that at high pressures the polyvinyl acetate chains are squeezed out of the monolayer into a substrate layer just below the rigid stearic acid film. A very high compressibility, apparently due to this process, occurs at spreading pressures between 16 and 18 dynes/cm. Nevertheless, Fig. 4 shows that data for this system are also well represented by theory for the infinitely viscoelastic monolayer model even in the transition region (velocity of propagation data were obtained at spreading pressures of 16.5 and 17.5 dynes/cm as well as at the spreading pressures shown, and were similar in character to results presented), indicating that the relaxation time for transfer of polyvinyl acetate from surface to substrate is large compared to the oscillation period even at the lowest frequency (185 cps) studied.

Results obtained with heptanoic acid soluble monolayers at two heptanoic acid concentrations are presented in Fig. 5. These data show rather severe scatter, particularly in the range 300-600 cps. The infinitely viscoelastic monolayer model represents the data as well as any model involving finite viscoelastic parameters, but the representation of the dependence of y_1 (and hence also the velocity of propagation) on frequency in particular is not very satisfactory and results at frequencies above 1000 cps are from 4% to 7% below theoretical expectations (velocities of propagation from 1.3% to 2.3% lower than theoretical). Using the data of King for dependence of surface tension of aqueous heptanoic acid solutions on concentration (16) the quantities k_e and $(\frac{\partial \gamma}{\partial c})_{c_0}$ can be estimated for solutions of surface tensions of 50.7 and 37.6 dynes/cm; values of k_e/γ are found to be 1.3 and 5.6 respectively, but the effect of diffusional transfer from solution to surface is such as

to cause u_2 to be considerably less than $(k_e^2 + \omega^2 k_v^2)^{1/2} / \gamma$ at both concentrations and at all frequencies studied. For $k_v = 0$, values of u_2 would range from 0.02 (100 cps, surface tension 37.6 dynes/cm) to 0.18 (1000 cps, surface tension 50.7 dynes/cm), with the lowest values corresponding to slightly viscoelastic films, and the highest values still sufficiently low that experiments should have clearly distinguished such films from the infinitely viscoelastic model. It is therefore again necessary to assume that either k_e is much greater than the inverse of the compressibility or that ωk_v is large compared to k_e over the frequency range studied. At concentrations studied the diffusional transfer is such that values of ωk_v correspond to a viscoelastic parameter θ_2 of nearly 45° , and with such a value of θ_2 values of u_2 ranging from 0.1 to 1 would lead to velocities of propagation substantially less and amplitude attenuations substantially greater than those for a rigid monolayer. The observed deviations are in this direction, but an explanation based on such values of u_2 would also imply that the deviations from the rigid monolayer model should decrease with increasing frequency, while in fact the deviations in the case of velocity of propagation increase with increasing frequency. This explanation of the deviations from the rigid monolayer model therefore can not be considered satisfactory.

CONCLUSIONS

Agreement between results and theory (3) appears adequate to justify the theory presented earlier. This indicates that the classical assumption of the continuity of the velocity vector field in the limit of the approach to the bounding surface is valid, and that it is unnecessary to postulate slip between surface film and subphase to represent

experimental results. In our opinion, some earlier theoretical treatments have erred in the character of approximations made in the solution of the complex determinant arising from the surface stress boundary conditions in the hydrodynamic problem. This determinant can be much simplified if Kelvin's equation is assumed to hold exactly, and this approximation has been used (17, 18). Particularly for viscoelastic films the error introduced by this approximation is of the same order as the reduced damping coefficient γ_2 , and leads to significantly higher values of γ_2 than a theory avoiding this approximation. Goodrich (19) does not present his handling of this point in detail, but his discussion suggests that he also has made this approximation, and if so his difficulty in representing damping coefficient data obtained for stearic acid and several alcohol monolayers is likely to be of this origin.

Except for stearic acid monolayers, it has been necessary to suppose either that the elastic constant k_e is large compared to the inverse of the compressibility, or else that the viscous parameter k_v is such that ωk_v is large compared to k_e over the range of frequencies studied. If the latter is true experiments at sufficiently low frequencies should lead to a transition to slightly viscoelastic monolayer characteristics; our present instrumentation is unfortunately poorly suited for experiments at frequencies much below 200 cps.

The techniques used in the present work should be applicable to the study of liquid-liquid interfaces. Modifications of the theoretical treatment would be necessary, but the general form of the theory has been indicated by Koussakov (20). It appears that lateral interactions in films at liquid-liquid interfaces are much smaller than the analagous interactions at the liquid-air interface.

Finally, these techniques may be suitable for study of adsorption kinetics. In principle, it should be only necessary to measure phase angle and wave amplitude as functions of time at constant probe separation to establish the variation of surface tension with time, and if these experiments were repeated at different frequencies, time dependence of viscoelastic properties could also be documented. Since the techniques are suitable for automatic recording this application might well bridge the gap between vibrating jet methods (for adsorption processes with millisecond half lives) and drop weight (for adsorption processes with half lives large compared to 1 second).

BIBLIOGRAPHY

1. Brown, R. C., Proc. Phys. Soc. (London) 48, 312 (1936);
Brown, R. C., Proc. Phys. Soc. (London) 48, 323 (1936).
2. Mann, J. A., and Hansen, R. S., J. Colloid Science, in press
(experimental).
3. Hansen, R. S., and Mann, J. A., Ibid., in press (theory).
4. Mann, J. A., and Hansen, R. S., Rev. Scientific Instruments, in
press.
5. Adam, N. K., The Physics and Chemistry of Surfaces, 3rd ed.
London, Oxford University Press, 1941.
6. Harkins, W. D., The Physics and Chemistry of Surface Films.
New York, N. Y., Reinhold Publishing Corporation, 1952.
7. Adamson, A. W., Physical Chemistry of Surfaces. New York,
N. Y., Interscience Publishers, Inc., 1960.
8. Davies, J. T., and Rideal, E. K., Interfacial Phenomena. New
York, N. Y., Academic Press, Inc., 1961.
9. La Mer, V. K., and Robbins, M. L., J. Colloid Sci. 15, 123 (1960).
10. Bull, H. B., J. Am. Chem. Soc. 67, 4 (1945).
11. Trurnit, H. J., J. Colloid Sci. 15, 1 (1960).
12. Zuidema, H. H., and Waters, G. W., Ind. Eng. Chem., Anal. Ed.
13, 312 (1941).
13. Lange, N. A., Handbook of Chemistry, 8th ed. Sandusky, Ohio,
Handbook Publishers, Inc., 1952.
14. Goodrich, F. C., Proc. Roy. Soc. (London) A260, 481-509 (1961).
15. Ries, H. E., and Walker, D. C., J. Colloid Sci. 16, 361 (1961).
16. King, H. H., Kansas State Agricultural College Tech. Bul. No. 9,
1922.

17. Levich, V., *Acta Physicochimica U.R.S.S.* 14, 307 (1941).
18. Dorrestein, R., *Proc. Koninkl. Ned. Akad. Wetenschap* B54, 260 (1951).
19. Goodrich, F. C., *Preprints, 36th National Colloid Symposium*, 1962.
20. Koussakov, M., *Acta Physicochimica U.R.S.S.* 19, 286 (1944).

FIGURE CAPTIONS

- Figure 1. Dependence of Kelvin Function $y_1 = \frac{\rho\omega^2}{\gamma k^3}$ and reduced amplitude attenuation $y_2 = \alpha/k$ on frequency for distilled water. Curves are theoretical for surfaces showing no viscoelasticity.
- Figure 2. Dependence of Kelvin Function $y_1 = \frac{\rho\omega^2}{\gamma k^3}$ and reduced amplitude attenuation $y_2 = \alpha/k$ on frequency for stearic acid and egg albumen monolayers on water. Curves are theoretical for infinitely viscoelastic monolayer.
- Figure 3. Dependence of Kelvin Function $y_1 = \frac{\rho\omega^2}{\gamma k^3}$ and reduced amplitude attenuation $y_2 = \alpha/k$ on frequency for propylene glycol monostearate and 1,3-dipalmitoyl glyceryl phosphoric acid monolayers on water. Curves are theoretical for infinitely viscoelastic monolayer.
- Figure 4. Dependence of Kelvin Function $y_1 = \frac{\rho\omega^2}{\gamma k^3}$ and reduced amplitude attenuation $y_2 = \alpha/k$ on frequency for 1:1 octadecanol-hexadecanol and stearic acid - polyvinyl acetate mixed monolayers. Curves are theoretical for infinitely viscoelastic monolayer. Both systems show very large equilibrium compressibilities for spreading pressures near 16 dynes/cm.
- Figure 5. Dependence of Kelvin Function $y_1 = \frac{\rho\omega^2}{\gamma k^3}$ and reduced amplitude attenuation $y_2 = \alpha/k$ on frequency for heptanoic acid solutions. Curves are theoretical for infinitely viscoelastic monolayer.

Figure 1. Dependence of Kelvin Function $y_1 = \frac{\rho \omega^2}{\gamma k^3}$ and reduced amplitude attenuation $y_2 = \alpha/k$ on frequency for distilled water. Curves are theoretical for surfaces showing no viscoelasticity.

Figure 2. Dependence of Kelvin Function $y_1 = \frac{\rho\omega^2}{\gamma k^3}$ and reduced amplitude attenuation $y_2 = \alpha/k$ on frequency for stearic acid and egg albumen monolayers on water. Curves are theoretical for infinitely viscoelastic monolayer.

Figure 3. Dependence of Kelvin Function $y_1 = \frac{\rho \omega^2}{\gamma k^3}$ and reduced amplitude attenuation $y_2 = \alpha/k$ on frequency for propylene glycol monostearate and 1,3-dipalmitoyl glyceryl phosphoric acid monolayers on water. Curves are theoretical for infinitely viscoelastic monolayer.

Figure 4. Dependence of Kelvin Function $y_1 = \frac{\rho\omega^2}{\gamma k^3}$ and reduced amplitude attenuation $y_2 = \alpha/k$ on frequency for 1:1 octadecanol-hexadecanol and stearic acid-polyvinyl acetate mixed monolayers. Curves are theoretical for infinitely viscoelastic monolayer. Both systems show very large equilibrium compressibilities for spreading pressures near 16 dynes/cm.

Figure 5. Dependence of Kelvin Function $y_1 = \frac{\rho\omega^2}{\gamma k^3}$ and reduced amplitude attenuation $y_2 = \alpha/k$ on frequency for heptanoic acid solutions. Curves are theoretical for infinitely viscoelastic monolayer.

END