

- (22) Sherman, P., "Rheology of Emulsions," Sherman, P., ed., Pergamon Press, New York, N. Y., 1963.
- (23) Sherman, P., *J. Soc. Chem. Ind. (London) Suppl.* **2**, 69, S70(1950).
- (24) Sherman, P., *Kolloid-Z.*, **165**, 156(1959).
- (25) McMahon, J. D., Hamill, R. D., and Petersen, R. V., *J. Pharm. Sci.*, **52**, 1163(1963).
- (26) Petersen, R. V., Hamill, R. D., and McMahon, J. D., *ibid.*, **53**, 651(1964).
- (27) Hamill, R. D., Olson, F. A., and Petersen, R. V., *ibid.*, **54**, 537(1965).
- (28) Bowles, R. L., Davie, R. P., and Todd, W. D., *Mod. Plastics*, **32**, 142(1955).
- (29) Runikis, J. O., Hall, N. A., and Rising, L. W., *J. Am. Pharm. Assoc., Sci. Ed.*, **47**, 758(1958).
- (30) Doolittle, A. K., "The Technology of Solvents and Plasticizers," John Wiley & Sons, Inc., New York, N. Y., 1954.
- (31) Eirich, F. R., "Rheology," vol. 1, Eirich, F. R., ed., Academic Press Inc., New York, N. Y., 1960.
- (32) Levius, H. P., and Drummond, F. G., *J. Pharm. Pharmacol.*, **5**, 743(1953).
- (33) Chong, C. W., Ericksen, S. P., and Swintosky, J. V., *J. Am. Pharm. Assoc., Sci. Ed.*, **49**, 547(1960).
- (34) Menczel, C., Rabenovitz, M., and Madjor, A., *Am. J. Pharm.*, **132**, 315(1960).
- (35) Appino, J. B., Christian, J. E., and Banker, G. S., *J. Pharm. Sci.*, **51**, 254(1962).
- (36) Wood, J. H., and Catalalos, G., *J. Soc. Cosmetic Chemists*, **14**, 147(1963).

Effect of Surfactant Concentration on the Interfacial Viscosity of a Nonaqueous System

By RICHARD D. HAMILL* and ROBERT V. PETERSEN

The interfacial viscosities of the glycerin-olive oil interface after either ammonia or 2-amino-2-methyl-1,3-propanediol (AMP) had been added were studied by means of a viscous traction interfacial viscometer. The amine concentrations used were 0.6, 2, and 6 mg. ammonia/100 ml., and 2, 6, and 20 mg. AMP/100 ml. The results indicate that more rigid films were produced at the interface as amine concentrations were increased. The original viscosities and the increased viscosities resulting from increased amine concentrations were as would be predicted from fatty acid films. However, viscosities were not so high as thought to be necessary for stability against coalescence in emulsions.

PREVIOUS STUDIES from this laboratory have demonstrated that nonaqueous emulsions of glycerin and olive oil can be prepared by means of anionic, cationic, or nonionic surfactants (1, 2). It has further been pointed out that a high degree of emulsion stability can be achieved with extremely low concentrations of saponifying amines such as ammonia or 2-amino-2-methyl-1,3-propanediol (AMP). Indeed, concentrations barely sufficient to produce monomolecular films of the amine soap at the interface produced stable emulsions (3).

The effect on emulsion stability of a rigid interfacial film as a mechanical barrier to coalescence has been studied by several investigators. In 1941, King (5) proposed that the strength and compactness of the interfacial film in an emulsion were the most important factors favoring stability. A year earlier, Schulman and Cockbain (6, 7) implied the necessity of high inter-

facial viscosity for emulsion stability by stating several conditions essential for optimum stability including the need for a "condensed" interfacial film. Becher (8) has also suggested that the formation of a rigid interfacial film is a mechanism in stabilizing emulsions. Sumner (10) supports this concept by suggesting that the mechanical strength of the film of emulsifying agent around the droplets is important. Blakey and Lawrence (11) found a partial correlation between emulsion stability and surface viscosity at the solution-air surface. More recently, the mechanical resistance of the film and emulsion stability have been related (12, 13).

Because of the remarkable stabilizing effect of ammonia and AMP and because it has been repeatedly suggested that a relation exists between emulsion stability and the interfacial viscosity and mechanical strength of the film in oil-water systems (4-13), it seemed important to study the interfacial viscosities of the glycerin-olive oil system containing varying concentrations of amine to determine if a similar relation exists which could help to explain the unusual stability of emulsions of these components.

EXPERIMENTAL

The term interfacial viscosity, as used throughout this study, is defined as the shear viscosity of a monolayer spread or adsorbed at the interface

Received April 20, 1966, from the College of Pharmacy, University of Utah, Salt Lake City, 84112.

Accepted for publication July 12, 1966.

Presented to the Basic Pharmaceutics Section, A.P.H.A. Academy of Pharmaceutical Sciences, Dallas meeting, April 1966.

Abstracted in part from a thesis submitted by Richard D. Hamill to the Graduate School, University of Utah, Salt Lake City, in partial fulfillment of Doctor of Philosophy degree requirements.

This investigation was supported in part by a grant from the University of Utah Research Fund.

* Fellow of the American Foundation for Pharmaceutical Education, 1963-1965. Recipient of the Josiah Kirby Lilly Memorial Fellowship, 1964-1965. Present address: Baxter Laboratories, Inc., Morton Grove, Ill. 60053.

between two liquids. The term surface viscosity, on the other hand, is the shear viscosity of a monolayer spread or adsorbed at the surface of a liquid (14). Both interfacial and surface viscosities have the dimensions MT^{-1} , instead of $ML^{-1}T^{-1}$ as for bulk viscosity (where M , L , and T represent mass, distance, in cm., and time, in sec., respectively), and are measured in units of Gm. sec. $^{-1}$ called "surface poise" (s.p.).

Interfacial viscosity was measured by means of the instrument shown in Fig. 1. Except for the diameter of the wire (0.078 cm. instead of 0.064 cm.) used to form the concentric rings and the driving mechanism (Bodine speed reduction motor and appropriate pulley arrangement), this instrument was constructed according to the specifications of the modified viscous traction interfacial viscometer of Davies and Mayers (15). The specifications of the instrument will be mentioned briefly. The two concentric stainless steel wire rings were held in place by the larger support rods

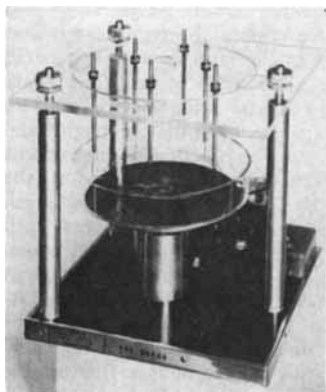


Fig. 1.—Interfacial viscometer.

attached to the upper plastic platform. Three wires of the same diameter as used for the rings were soldered to each ring and made to lie in the plane of the rings for a short distance (about 1.5 cm.) before they were bent upward and soldered to the support rods. The diameters of the outer and inner rings were 12.5 and 11.6 cm., respectively. A Pyrex dish, 18.5 cm. in diameter and 4 cm. high, was centered on the turntable and held the liquids which formed the interface to be studied. The turntable rotated at 1 rev. in 38 sec. The wire rings were held stationary by both the support rods and the upper platform, but the platform could be adjusted, thereby raising and lowering the rings to the desired position.

The methods employed in the use of the instrument were also patterned after those described by Davies and Mayers (15). The results obtained are dependent upon the amount of retardation of the film flowing in the canal when the interface is clean and when an additive is present. To measure retardation, talc particles were placed at the interface and the time for 1 rev. was measured. The rings were raised slightly above the interface producing a meniscus, which acted as a trough to insure that the talc particles remained in the canal.

In order to determine if the difference in wire

diameter modified the calibration curve used by Davies and Mayers when applied to this instrument, three experiments were performed. First, the two interfaces (benzene/water and ethyl acetate/water) utilized by the original investigators when calibrating their instrument at the oil-water interface were formed and duplicate results were obtained. Second, Davies and Mayers reported interfacial viscosities of monolayers adsorbed from $4 \times 10^{-3} M$ sodium lauryl sulfate solutions at the benzene-water interface as 1.5×10^{-4} s.p. at 20° and as 1×10^{-4} s.p. at 22° . The viscometer constructed for this study gave an interfacial viscosity of 1.2×10^{-4} s.p. at 21° . Third, Davies (4) reported the surface viscosity of stearic acid on 0.01 N HCl as 6.25×10^{-4} s.p. at 20.1° . A similar film was used to verify this value with the present instrument. A benzene solution of stearic acid was applied to the surface of 0.01 N HCl using a micrometer syringe. Surface area calculations were corrected for the small area occupied by the wire rings. A surface viscosity of 6.5×10^{-4} s.p. was obtained when measuring this film. These data suggest that the results obtained with this instrument are remarkably similar to those obtained by Davies and Mayers and that their calibration curve can be used within the range of duplicate results.

Six solutions of amine in glycerin were prepared to correspond with the concentrations of ammonia (0.6, 2, and 6 mg./100 ml.) and 2-amino-2-methyl-1,3-propanediol (AMP) (2, 6, and 20 mg./100 ml.) used in emulsions studied and reported in a separate publication (16). These concentrations were based on the total amount of olive oil and glycerin contained in the dish. The ratio of glycerin to olive oil was 60:40 analogous to a phase volume of 0.40 used in the olive oil-in-glycerin emulsions previously studied (16).

The mean time of 1 rev. at the clean glycerin-olive oil interface was determined. Following this, mean revolution times were measured at the glycerin-olive oil interface after varying amounts of ammonia or AMP had been added. All determinations were made at 20° .

Each interface was measured within a few minutes after it was formed and at intervals over the next 2 hr. Several revolutions were timed and averaged to obtain the mean time of 1 rev. The mean time of the clean glycerin-olive oil interface was subtracted from the mean time of each sample to determine the amount of retardation. The calibration curve (Fig. 2) was then used to obtain the interfacial viscosity in s.p.

RESULTS

Table I lists the results of the interfacial viscosity studies at the glycerin-olive oil interface.

When the interface was clean (no amine added) the mean time of 1 rev. was 171 sec., corresponding to no retardation and therefore, no interfacial viscosity. Upon the addition of 0.6 mg. ammonia/100 ml. to the glycerin phase, the mean time of 1 rev. at the interface was 185 sec. representing a 14-sec. retardation. This was equivalent to an interfacial viscosity of 1.2×10^{-4} s.p. The mean revolution time rose to 204 sec. with the addition of 2 mg. ammonia/100 ml. to the glycerin phase. This represented a retardation of 33 sec. and a

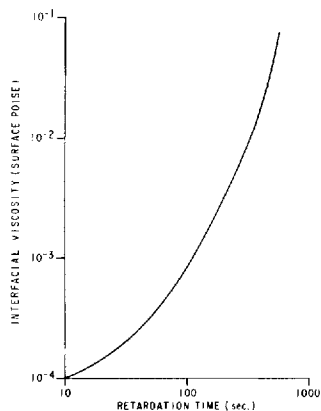


Fig. 2.—Calibration curve for the interfacial viscometer. [After Davies and Mayers (15).]

viscosity of 2.2×10^{-4} s.p. A 52-sec. retardation time was shown when 6 mg. ammonia/100 ml. was added to glycerin. This corresponded to a mean revolution time of 223 sec. and an interfacial viscosity of 3.4×10^{-4} s.p.

Upon the addition of 2, 6, and 20 mg. AMP/100 ml. to the glycerin phase, mean revolution times of 206, 217, and 225 sec., respectively, were obtained; these represent retardation times of 35, 46, and 54 sec., and interfacial viscosities of 2.3×10^{-4} , 3.0×10^{-4} , and 3.6×10^{-4} , respectively.

All interfaces formed with either ammonia or AMP in the glycerin phase showed constant mean revolution times within 30 min.

DISCUSSION

This study was undertaken to measure the effects of various concentrations of ammonia or AMP upon the interfacial viscosities of the glycerin-olive oil interface.

The existence of surface viscosity was first observed by Plateau in 1869 (14). Plateau observed that a fluid surface exhibited resistance to deformation or flow from the difference in damping rates of a compass needle oscillating on the surface and in the interior of a liquid. Since that time several methods for the measurement of surface

and interfacial viscosities have been developed (4, 15, 17-22). However, the modified "flow through a canal" method of Davies and Mayers was selected for this study because of several inherent advantages. Ewers and Sack (21) have discussed the validity of the "flow through a canal" technique with soluble layers. They pointed out that where surface pressure is applied to soluble layers, part of the adsorbed film merely dissolves in the interior of the liquid instead of passing through the canal. The "viscous traction" modification of Davies (4) and Davies and Mayers (15) overcomes this disadvantage by allowing the liquid substrate to cause the film to move. Another advantage in the use of this modification is that the width of the canal can be varied and made as narrow as required to increase the sensitivity when working with monolayers of very low viscosity. Joly (14) states that this method is considered best for measuring films of low Newtonian viscosity. The existence of both Newtonian viscosity and viscosity of a low magnitude (10^{-4} s.p.) can easily be established for the glycerin-olive oil system. The very presence of olive oil with its free fatty acid content makes it reasonable to hypothesize that the surfactant found at the interface is a fatty acid type. Furthermore, Joly (23) states that practically all monolayers of fatty acids and triglycerides are Newtonian and are of a low order of magnitude.

The disadvantage in the use of this instrument involves the mathematical interpretation of the hydrodynamics of the process. Since this is extremely complicated, Davies and Mayers calibrated their instruments using films of known surface viscosities. After calibrating the instrument at the air-water surface, they applied it to the oil-water interface. In the first instance, a benzene water interface was measured and flow in the canal was found to take only 10 sec. longer than at the clean air-water surface. When ethyl acetate was used in place of benzene, 1 rev. took only 5 sec. longer. Because of this approximate equality, they concluded that the viscous drag, which the rotating oil exerts on the tale in the canal, balances the extra drag on the interface by the stationary canal walls *via* the adjacent oil. Therefore, the same calibration curve which was determined at the air-water surface was used at the oil-water interface. Davies

TABLE I.—INTERFACIAL VISCOSITY OF GLYCERIN-OLIVE OIL INTERFACE AFTER THE ADDITION OF EITHER AMMONIA OR AMP

Additive	Mean Time of 1 rev., sec.	Retardation, sec.	Interfacial Viscosity, $\times 10^{-4}$ s.p.
No additive	171 (170-175) ^a	0	0
0.6 mg. NH ₃ /100 ml.	185 (182-187)	14	1.2
2 mg. NH ₃ /100 ml.	204 (203-205)	33	2.2
6 mg. NH ₃ /100 ml.	223 (221-223)	52	3.4
2 mg. AMP/100 ml.	206 (202-209)	35	2.3
6 mg. AMP/100 ml.	217 (215-219)	46	3.0
20 mg. AMP/100 ml.	225 (223-229)	54	3.6

^a Numbers in parentheses indicate the range of observed revolution times from which mean time was calculated.

and Mayers claim that their instrument can be used to study interfacial viscosities from 10^{-4} to 10^{-1} s.p. The only portion of the curve utilized in this study was between 10^{-4} and 10^{-3} s.p., which was essentially within the range where duplicate results were obtained with known films.

The results obtained demonstrate that there is a measurable increase in viscosity when the concentration of ammonia is raised from 0.6 mg./100 ml. to 6 mg./100 ml. At 0.6 mg./100 ml. the interfacial viscosity was 1.2×10^{-4} s.p. This increased to 2.2×10^{-1} s.p. at 2 mg./100 ml. and rose again at 6 mg./100 ml. to 3.4×10^{-4} s.p.

The addition of AMP to the glycerin phase showed a similar increase in interfacial viscosity. At 2 mg./100 ml., the interfacial viscosity was 2.3×10^{-4} s.p. The interfacial viscosity rose to 3.0×10^{-4} at 6 mg./100 ml. and to 3.6×10^{-4} s.p. at 20 mg./100 ml.

Davies and Rideal (24) state that monolayers of fatty acid esters which give "gaseous" films of great areas are characterized by Newtonian flow and low viscosities (10^{-5} to 10^{-4} s.p.). Monolayers of higher fatty acid esters and of oleic acid also show Newtonian flow and viscosities of this order, but show an increase in viscosity as the concentration is increased and the available surface area decreased producing a more "condensed" film.

Davies (25) reports that an interfacial viscosity of at least 10^{-2} s.p. seems to be required if the interfacial film is not to allow coalescence during the close approach of two droplets. The results of this study indicate that a more rigid film is produced at the interface as the amine concentration is increased. The results also indicate that the orders of magnitude of the viscosities and their increases over the concentrations studied were similar to viscosities predictable from Newtonian fatty acid films, but that they were not so large as Davies suggests is needed for coalescence inhibition.

The knowledge that a more viscous interfacial film is present in the glycerin-olive oil system is not meaningful in itself, but when correlated with published work on the stability of glycerin-olive oil emulsions (16), a significant relation can be hypothesized. When either ammonia or AMP was employed in the emulsion system, stability as seen by droplet size distribution data, increased as the added amine was increased. This study then has demonstrated that stability can be achieved in these emulsions with interfacial viscosities which are on the order of 100 times lower than that considered necessary.

SUMMARY

A viscous traction interfacial viscometer, patterned after the one described by Davies and

Mayers, was used to measure interfacial viscosity at the glycerin-olive oil interface after either ammonia or 2-amino-2-methyl-1,3-propanediol (AMP) had been added. The concentrations of amine employed corresponded with those used in an olive oil-glycerin emulsion stability study.

The results indicate that a more rigid film was produced at the interface as the amine concentration was increased. The interfacial viscosity increased from 1.2×10^{-4} s.p. at 0.6 mg. ammonia/100 ml. to 3.4×10^{-4} s.p. at 6 mg./100 ml. The interfacial viscosity of the AMP film increased similarly. At 2 mg. AMP/100 ml., the interfacial viscosity was 2.3×10^{-4} s.p. This rose to 3.6×10^{-4} s.p. at 20 mg./100 ml.

The viscosities measured and the increases seen are as would be predicted from known fatty acid films. However, the viscosities were on the order of 100 times smaller than that thought necessary for stability against coalescence in emulsions.

REFERENCES

- (1) McMahon, J. D., Hamill, R. D., and Petersen, R. V., *J. Pharm. Sci.*, **52**, 1163(1963).
- (2) Petersen, R. V., Hamill, R. D., and McMahon, J. D., *ibid.*, **53**, 651(1964).
- (3) Hamill, R. D., Olson, F. A., and Petersen, R. V., *ibid.*, **54**, 537(1965).
- (4) Davies, J. T., "Second International Congress of Surface Activity," vol. I, Schulman, J. H., ed., Butterworth Scientific Publications, London, England, 1957, p. 220.
- (5) King, A., *Trans. Faraday Soc.*, **37**, 168(1941).
- (6) Schulman, J. H., and Cockbain, E. G., *ibid.*, **36**, 651(1940).
- (7) *Ibid.*, **36**, 661(1940).
- (8) Becher, P., *Am. Perfumer Cosmetics*, **77**, 21(1962).
- (9) Shotton, E., and White, R. F., "Rheology of Emulsions," Sherman, P., ed., Pergamon Press, New York, N. Y., 1963, p. 59.
- (10) Sumner, C. G., *Chem. Ind.*, **1960**, 1066.
- (11) Blakey, B. C., and Lawrence, A. S. C., *Discussions Faraday Soc.*, **18**, 268(1954).
- (12) Taubman, A. B., and Koretkii, A. F., *Kolloid Zh.*, **20**, 676(1958); through *Chem. Abstr.*, **53**, 11948e(1959).
- (13) Rehbinder, P., and Taubman, A., *Proc. Third Intern. Congr. Surface Activity*, **1**, 209(1960).
- (14) Joly, M., "Recent Progress in Surface Science," vol. 1, Danielli, J. F., Pankhurst, K. G. A., and Riddiford, A. C., eds., Academic Press Inc., New York, N. Y., 1964, p. 1.
- (15) Davies, J. T., and Mayers, G. R. A., *Trans. Faraday Soc.*, **56**, 691(1960).
- (16) Hamill, R. D., and Petersen, R. V., *J. Pharm. Sci.*, **55**, 1268(1966).
- (17) Cheesman, D. F., and Sten Knudsen, O., *Biochim. Biophys. Acta*, **33**, 158(1959); through *Chem. Abstr.*, **53**, 17213d(1959).
- (18) Langmuir, I., *Science*, **84**, 379(1936).
- (19) Langmuir, I., and Schaeffer, V. J., *J. Am. Chem. Soc.*, **59**, 2400(1937).
- (20) Harkins, W. D., and Myers, R. J., *Nature*, **140**, 465(1937).
- (21) Ewers, W. E., and Sack, R. A., *Australian J. Chem.*, **7**, 40(1954).
- (22) van Wazer, J. R., *J. Colloid Sci.*, **2**, 223(1947).
- (23) Joly, M., *ibid.*, **11**, 519(1956).
- (24) Davies, J. T., and Rideal, E. K., "Interfacial Phenomena," Academic Press Inc., New York, N. Y., 1963, p. 261.
- (25) Davies, J. T., "Recent Progress in Surface Science," vol. 2, Danielli, J. F., Pankhurst, K. G. A., and Riddiford, A. C., eds., Academic Press Inc., New York, N. Y., 1964, p. 129.