Effects of Aging and Surfactant Concentration on the Rheology and Droplet Size Distribution of a Nonaqueous Emulsion

By RICHARD D. HAMILL* and ROBERT V. PETERSEN

Six olive oil-in-glycerin emulsions were prepared wherein ammonia and 2-amino-2-methyl-1,3-propanediol (AMP), in various concentrations, served as saponifying agents. Six-tenths, 2, and 6 mg. ammonia/100 ml. and 2, 6, and 20 mg. AMP/100 ml. were used in making the emulsions. The emulsions were stored at room temperature (25°), and droplet size, rheology, and emulsion stability studied on days 1, 2, 4, 7, 14, 30, and 60. Droplet size, as measured from photographs taken by phase contrast photomicrography, were inversely related to amine concentration. Growth in droplet size over the period of study was more striking in AMP emulsions than in ammonia emulsions. Rheology studies with the Brookfield LVT viscometer revealed the existence of non-Newtonian pseudoviscous flow. The emulsions were very stable, as indicated by logarithmic graphs of viscosity and time. It is suggested that the data may be extrapolated to predict viscosity over longer time periods.

WHEN AN EMULSION is aged there is usually a distinct growth in droplet size before the dispersed phase separates in bulk (1). This growth can be attributed to coalescence between neighboring droplets and has been characterized as following first-order kinetics (2, 3).

Some of the factors which have an effect on droplet size in an emulsion are the method of preparation, phase–volume ratio, temperature during mixing, viscosity (4-8), and surfactant type and concentration (9). Conversely, the effects that droplet size and droplet size distribution have on emulsion viscosity have been explored. For example, the effects of homodispersity (10-14), flocculation (15-21), surfactant properties and concentration (22), and phase–volume relative to surfactant concentration (23, 24) on viscosity in oil–water emulsions have been studied and reported.

Previous reports (25, 26) have described the emulsifying effects of several ionic and nonionic surfactants on the nonaqueous, binary, immiscible system, glycerin and olive oil. More recently (27) this system was studied with regard to the effect of surfactant concentration on the effective size of two anionic amine surfactants formed *in situ* by the combination of either ammonia or 2-amino-2-methyl-1,3-propanediol (AMP) with the free fatty acids of olive oil.

The present study was designed to learn more about the stability of this emulsion system by examining the effects of aging and amine concentration on both rheology and droplet size distribution.

EXPERIMENTAL

Six olive oil-glycerin emulsions were prepared with varying concentrations of amine. Samples 1, 2, and 3 contained 0.6, 2, and 6 mg. of ammonia/100 ml. of emulsion, respectively; whereas samples 4, 5, and 6 contained 2, 6, and 20 mg. of AMP/100 ml. of emulsion, respectively. These concentrations were chosen because 0.6 mg. of ammonia/100 ml. and 2 mg. AMP/100 ml. correspond to the minimum amine concentrations needed for stable emulsifications at phase volumes of 0.40 as previously reported (27). Concentrations of 6 mg. of ammonia/100 ml. and 20 mg. AMP/100 ml. represent a tenfold increase above these minima. The two remaining samples contained concentrations intermediate between the minimum concentrations and the tenfold increase. The olive oil and glycerin used in making the emulsions and the order of mixing were the same as those previously described (25-27). All emulsions were made with phase volumes of 0.40. Emulsion type was confirmed by the phase dilution method.

The emulsions were stored at room temperature (25 ± 2°) for 2 months. A testing schedule was established wherein the six samples were tested at days 1, 2, 4, 7, 14, 30, and 60. Day 1 corresponds with the day the emulsions were made.

Photographs were taken by means of phase contrast photomicrography on the days chosen in the testing schedule. A Wild phase contrast microscope providing 480× magnification and equipped with a Polaroid camera was used. The wavelength of the light source was 475 mμ.

A glass microscope slide was prepared by placing a drop of emulsion on the slide after which a cover glass was gently rested on the emulsion. Care was taken not to apply any pressure on the sample other than that exerted by the weight of the cover

glass. Pressure on the cover glass could cause distortions or force some droplets to coalesce in the emulsion, thus altering the droplet diameter results. The prepared slide was set aside for 1 hr. This time period was required to allow movement in the sample virtually to stop so that a clear photomicrograph could be obtained. The low intensity of the light source used in this type of microscopy required a several-second exposure time. Photographic prints were obtained using Polaroid Polapan 200 film. The photograph taken was immediately available for inspection to insure a picture of best possible clarity.

Two or three 1-in. squares were arbitrarily selected from each photomicrograph and the diameters of 200 to 300 droplets were classified within these areas. The average droplet diameter (D_m) was calculated using Eq. 1 (22).

$$D_m = \sqrt[3]{\frac{\Sigma n D^3}{\Sigma n}} \qquad \text{(Eq. 1)}$$

where n is the number of droplets with a diameter of D.

The rheology of each emulsion was studied on the test days using a Brookfield LVT viscometer. Day 120 also was included in the rheology testing schedule. Each sample was poured into the test container which was then placed into a constant-temperature water bath, maintained at $25 \pm 0.2°$, and allowed to equilibrate for 45 min. Spindle No. 2 provided with the Brookfield viscometer was chosen for testing the emulsions because it allowed the widest range of scale readings over a large number of r.p.m. (shear rate). Dial readings (shear stress) at spindle speeds of 0.6, 1.5, 3, and 6 r.p.m. were recorded for each sample. A test was conducted to determine the presence of thixotropy by running the viscometer at 60 r.p.m. for 10 min. after having measured speeds from 0.6 up to 6 r.p.m. After this period of time the dial readings were again recorded, but this time from 6 down to 0.6 r.p.m. In samples where thixotropy was present, the amount of standing time required before the "up" readings could be duplicated was noted.

To utilize effectively the Brookfield viscometer on non-Newtonian materials, various methods of calculation have been proposed (28, 29). The method described by Runikis *et al.* (29) takes into account the entire flow data obtainable with the Brookfield instrument. Their "*n* value" method utilizes Eq. 2 which they derive and explain.

$$\text{viscosity} = \frac{(K_B)\,(n)\,(\text{scale reading})}{(\text{r.p.m.})} \qquad \text{(Eq. 2)}$$

Since $K_B = 300$ when spindle No. 2 is used with the Brookfield LVT viscometer, Eq. 2 becomes

$$\text{viscosity} = \frac{300\,(n)\,(\text{scale reading})}{(\text{r.p.m.})} \qquad \text{(Eq. 3)}$$

A logarithmic plot of r.p.m. *versus* scale reading is a convenient method of calculating n since the reciprocal of the slope of the line formed in such a plot equals n.

All viscosity data reported in this study have been calculated from Brookfield data using Eq. 3 and recorded in centipoise (cps.).

A brief definition of some rheology terms which will appear in subsequent parts of this paper is necessary to avoid confusion later. Non-Newtonian flow can be classified according to the presence or absence of a yield value. A yield value represents that amount of force necessary before a liquid begins to flow. If a material does not exhibit a yield value, it is referred to as viscous flow and if it does, it is called plastic flow (30, 31). This division of flow type is rarely referred to in pharmaceutical literature, but it represents more precisely the fundamental types of flow with less ambiguity. According to this definition, a material which thins out or becomes less viscous as the rate of shear is increased is referred to as pseudoviscous rather than pseudoplastic, a term more commonly employed. The term pseudoplastic is reserved for that type of flow which becomes less viscous upon an increase in shear rate, but in addition, also exhibits a yield value. Dilatant materials, which become more viscous upon an increase in shear rate, must be identified further as dilatant-viscous or dilatant-plastic.

RESULTS

The effects of shear rate and age on the viscosity of the ammonia samples are shown in Table I. In sample 1 (0.6 mg. ammonia/100 ml.) the viscosity on day 1 at 0.6 r.p.m. was 3700 cps.; however, as the rate increased to 6 r.p.m. the viscosity dropped to 3630 cps. The influence of shear rate on viscosity became more marked in samples 2 (2 mg. ammonia/100 ml.) and 3 (6 mg. ammonia/100 ml.). Sample 2 decreased 220 cps. going from 3860 cps. at 0.6 r.p.m. to 3640 cps. and 6 r.p.m. Sample 3 exhibited a decline of 530 cps. as the rate was increased over the same interval. There were individual variations in each sample over the period of study, but no meaningful pattern could be defined.

Table I also shows that thixotropy appears to have developed by day 14 in sample 1. Although it could not be demonstrated on day 30, it appeared again on days 60 and 120. Samples 2 and 3 did not appear to display thixotropy until day 60, but after it developed it appeared to remain throughout the duration of the study.

The effect of shear rate on viscosity is further illustrated in Table II. The decrease in viscosity when the shear rate was increased from 0.6 to 6 r.p.m. is listed for each sample according to the day on which it was determined. The last column represents the mean decrease in viscosity for each sample. As shown in the table, the mean decrease in viscosity of sample 1 was 210 cps., whereas that for sample 3 was 590 cps. As was expected, the mean decrease in viscosity of sample 2 was intermediate to these values (340 cps.). Thus, there appears to be an inverse relation between amine concentration and susceptibility of the emulsions to shear rate.

Table III shows the effects of shear rate and age on the viscosities of the AMP emulsions. Pseudoviscous flow was also displayed by these emulsions. The influence of shear rate on the viscosities of samples 4, 5, and 6 (corresponding to 2, 6, and 20 mg. AMP/100 ml., respectively) is demonstrated in the same manner as for samples 1, 2, and 3. Sample 4 decreased in viscosity 130 cps. (from 3720 to 3590 cps.) as the shear rate was increased from 0.6 to 6 r.p.m. The effect of shear rate on viscosity

TABLE I.—EFFECT OF SHEAR RATE AND AGE ON THE VISCOSITY OF AMMONIA[a] EMULSIONS

Sample	Shear Rate (Spindle Speed, r.p.m.)	Day 1	Day 2	Day 4	Day 7	Viscosity, cps.[b] Day 14	Day 30	Day 60	Day 120
1	0.6	3700	4070	4060	4000	4000[c] / 3560	3960	3950 / 3320	4090 / 3790
	1.5	3680	3920	3920	3910	3850 / 3450	3810 / 3790	3810 / 3270	4030 / 3850
	3	3670	3860	3880	3840	3780 / 3400	3750 / 3730	3770 / 3200	3930 / 3800
	6	3630	3820	3840	3810	3730 / 3430	3720 / 3690	3740 / 3230	3890 / 3790
2	0.6	3860	4150	4270	4250	4060	4010	4010	4010 / 3620
	1.5	3750	3850	4060	4040	3850	3770	3770 / 3710	3830 / 3440
	3	3660	3750	3990	3980	3750	3710	3700 / 3640	3790 / 3360
	6	3640	3660	3920	3920	3710	3650	3650 / 3590	3720 / 3300
3	0.6	4250	4320	4530	4470	4320	4320	4230 / 4020	4470 / 4340
	1.5	3940	4000	4200	4160	3990	3950	3880 / 3650	4190 / 4000
	3	3810	3850	4020	4020	3830	3810	3670 / 3460	4020 / 3840
	6	3720	3750	3920	3910	3720	3700	3530 / 3350	3930 / 3730

[a] Samples 1, 2, and 3 contain 0.6, 2, and 6 mg./100 ml., respectively. [b] Viscosity measured with the Brookfield viscometer is reproducible to ±1%. [c] Thixotropy is represented by two figures for the same day and spindle speed. The upper figure represents the "up" viscosity determined when the spindle speed was increased from 0.6 to 6 r.p.m. The lower figure represents the "down" viscosity determined when the spindle speed was decreased from 6 to 0.6 r.p.m.

TABLE II.—VISCOSITY DECREASE IN AMMONIA[a] EMULSIONS RESULTING FROM SHEAR RATE INCREASE FROM 0.6 TO 6 r.p.m.

Sample	1	2	4	Day Examined 7	14	30	60	120	Mean Decrease
1	70	250	240	190	270	240	210	200	210
2	220	490	350	330	350	360	360	290	340
3	530	570	610	560	600	620	700	540	590

[a] Samples 1, 2, and 3 contain 0.6, 2, and 6 mg./100 ml., respectively.

was not as apparent in samples 4 and 5 as it was in samples 1 and 2; however, sample 6 showed a marked effect when compared with sample 4. Over the same shear rate interval sample 6 decreased 470 cps. The effect of shear rate on viscosity also varied with age. These variations did not follow a meaningful pattern, however.

Thixotropy appeared on day 14 in all AMP emulsions and continued through day 120 in sample 4 but could not be demonstrated in sample 5 on day 30 nor in sample 6 on day 120. In each case where thixotropy was present, the emulsion showed complete structural recovery within 2 hr. after the test.

Table IV, constructed like Table II, illustrates the net effect of viscosity decrease with shear rate for each AMP sample according to age. Sample 4 showed a mean decrease of 240 cps. There was no

change in the mean viscosity decrease between samples 4 and 5. Sample 6 does show greater mean decrease in viscosity than shown for samples 4 and 5. These data are consistent with those of the ammonia emulsions.

The effect of age on the droplet size in each emulsion studied is shown in Table V. The figures listed show the droplet size as per cent within a size class on the day examined for each sample studied. Upon inspection of the data for sample 1 it is easily seen that the per cent of droplets less than 0.5 μ decreased from 2.5 on day 1 to 0.6 on day 60, whereas the per cent of droplets 1.0 μ increased from 94.3 on day 1 to 96.0 on day 60. There was no significant change in the per cent of droplets with a diameter of 2.0 μ. Sample 2 shows the same pattern but to a lesser extent. Since the magnification in the photomicrographs was 480×,

TABLE III.—EFFECT OF SHEAR RATE AND AGE ON THE VISCOSITY OF AMP[a] EMULSIONS

Sample	Shear Rate (Spindle Speed, r.p.m.)	Day 1	Day 2	Day 4	Day 7	Day 14	Day 30	Day 60	Day 120
4	0.6	3720	3720	4140	4090	4000[c] / 3820	4140 / 3960	4110 / 3950	3980 / 3840
	1.5	3630	3670	4010	4010	3910 / 3760	4030 / 3730	3930 / 3750	3710 / 3620
	3	3600	3620	3960	3960	3840 / 3690	3950 / 3610	3890 / 3680	3510
	6	3590	3600	3900	3910	3780 / 3650	3900 / 3680	3820 / 3630	3470
5	0.6	3730	3500	3920	3870	3830 / 3520	3640	3770 / 3140	3920
	1.5	3690	3390	3780	3780	3650 / 3330	3490	3590 / 3060	3760 / 3720
	3	3620	3380	3700	3710	3510 / 3270	3440	3550 / 2980	3700 / 3680
	6	3590	3340	3660	3690	3410 / 3250	3410	3510 / 2960	3670 / 3640
6	0.6	4070	3720	4340	4290	4390 / 4160	4390 / 4310	4260 / 3960	4390
	1.5	3830	3610	4080	4060	4040 / 3870	4080 / 4020	3980 / 3760	4040
	3	3670	3630	3970	3940	3920 / 3750	3980 / 3900	3890 / 3630	3950
	6	3600	3520	3890	3890	3830 / 3670	3880 / 3820	3830 / 3580	3880

[a] Samples 4, 5, and 6 contain 2, 6, and 20 mg./100 ml., respectively. [b] Viscosity measured with the Brookfield viscometer is reproducible to ±1%. [c] Thixotropy is represented by two figures for the same day and spindle speed. The upper figure represents the "up" viscosity determined when the spindle speed was increased from 0.6 to 6 r.p.m. The lower figure represents the "down" viscosity determined when the spindle speed was decreased from 6 to 0.6 r.p.m.

TABLE IV.—VISCOSITY DECREASE IN AMP[a] EMULSIONS RESULTING FROM SHEAR RATE INCREASE FROM 0.6 TO 6 r.p.m.

Sample	1	2	4	7	14	30	60	120	Mean Decrease
4	130	120	240	180	220	240	290	510	240
5	140	160	260	180	420	230	260	250	240
6	470	200	450	400	560	510	430	510	440

[a] Samples 4, 5, and 6 contain 2, 6, and 20 mg./100 ml., respectively.

1 mm. was equivalent to 1.92 μ. The droplets in sample 3 were so small (in the range of 0.25 mm.) that they were impossible to measure; consequently, droplet size could not be obtained. It can be stated, however, that the droplets in this sample were less than 0.5 μ.

The emulsion having the lowest concentration of AMP is sample 4. As aging occurs, droplet size distribution appears as a decrease in per cent of droplets in smaller sizes and as an increase of larger sizes. The droplet size range narrows in sample 5; in sample 6 the droplet size became so small (as it did in sample 3) that a count could not be made. The droplet size range in sample 6 fell entirely below 0.5 μ.

The mean droplet size is reported in Table VI for each sample on the day it was determined. This table shows that even though a significant rise in droplet size with age cannot be demonstrated, the increase in mean droplet size with increased amine concentration is readily apparent.

DISCUSSION

It has been said that, with very few exceptions, all emulsion systems display some type of non-Newtonian flow characteristics especially when the phase volume exceeds 0.4 to 0.5 (23). The emulsions examined in this study proved no exception to this statement. A pronounced pseudoviscous type flow with the appearance of thixotropy was seen during the study. Thixotropy has been attributed to the formation of extended flocculated networks capable of giving the emulsion necessary structural properties before thixotropy can be seen (15, 16). Since flocculation is an important factor (15–21), its effects are seen to some extent in most

emulsions. Thus, it was not unexpected to see thixotropy displayed in all of the emulsions used in this study.

The increased influence of shear rate on viscosity as the rate was increased, as shown in both the ammonia and AMP emulsions, can undoubtedly also be explained on the basis of increased interaction between droplets or between the droplets and the dispersion medium.

The over-all increase in viscosity as the concentration of amine was increased agrees with previously cited work by Sherman (22). He concluded that the emulsifier can influence emulsion viscosity in several ways depending on its solubility in the two liquid phases, its chemical composition, the concentration used, and the physical properties of the film adsorbed around the droplets. The latter property has been studied on nonaqueous systems and will be described in a separate publication.

The effects of droplet size are also important here. A decreased mean droplet size corresponds to an increased total interfacial area. Both a decreased mean droplet size and an increased homodispersity was seen in the ammonia emulsions and also in the AMP emulsions. The effect of this on viscosity has been explained on the basis of a more uniform droplet size offering more resistance to flow, thus increasing viscosity (10), and by an increased interaction among droplets due to an increased interfacial area (12) with the effect being more pronounced when droplet dispersity becomes more uniform (13, 14).

Levius and Drummond (32) found that droplet size frequency analysis yielded more complete and reliable information about the internal state of the emulsion than was obtained from mean droplet size data only. This is in agreement with the results presented in Tables V and VI. The mean droplet size of each sample listed in Table VI gives the impression that little growth occurs between days 1 and 60. Table V reveals that droplet growth did continue through the entire period of study.

TABLE V.—EFFECT OF AGE ON DROPLET SIZE[a]

Diam., μ	1	2	4	Day Examined 7	14	30	60
Sample 1, 0.6 mg. NH₃/100 ml.							
<0.5	2.5	2.6	4.3	3.5	3.2	0.8	0.6
1.0	94.3	94.4	92.6	92.3	93.9	95.9	96.0
2.0	3.2	3.0	3.1	4.2	2.9	3.3	3.4
Sample 2, 2 mg. NH₃/100 ml.							
<0.5	95.5	95.5	95.5	94.3	94.3	94.3	94.4
1.0	4.5	4.5	4.6	5.7	5.7	5.7	5.6
Sample 3, 6 mg. NH₃/100 ml.							
<0.5	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Sample 4, 2 mg. AMP/100 ml.							
1.0	45.1	40.4	34.5	31.5	32.2	30.2	34.0
2.0	52.1	54.9	59.3	60.1	60.2	61.8	57.3
3.0	2.8	4.3	5.7	8.4	7.4	8.1	8.7
4.0	. . .	0.4	0.5	. . .	0.4	. . .	. . .
Sample 5, 6 mg. AMP/100 ml.							
<0.5	42.6	41.6	34.7	31.6	27.6	21.5	22.3
1.0	57.4	58.4	64.9	67.0	71.9	77.9	77.3
2.0	. . .	. . .	0.4	1.0	0.5	0.5	0.4
Sample 6, 20 mg. AMP/100 ml.							
<0.5	100.0	100.0	100.0	100.0	100.0	100.0	100.0

[a] Distribution is represented as per cents of total droplets measured in each size class.

TABLE VI.—EFFECT OF CONCENTRATION ON MEAN DROPLET SIZE[a]

Sample[b]	1	2	4	Day Examined 7	14	30	60
1	2.04	2.04	2.04	2.05	2.04	2.05	2.05
2	0.80	0.80	0.81	0.84	0.84	0.84	0.84
3				Less than 0.5			
4	3.36	3.53	3.65	3.74	3.73	3.74	3.73
5	1.61	1.62	1.70	1.77	1.77	1.80	1.79
6				Less than 0.5			

[a] Numbers represent droplet diameters calculated in microns using Eq. 1.   [b] Samples 1, 2, and 3 contain 0.6, 2, and 6 mg. NH₃/100 ml., respectively.   Samples 4, 5, and 6 contain 2, 6, and 20 mg. AMP/100 ml., respectively.
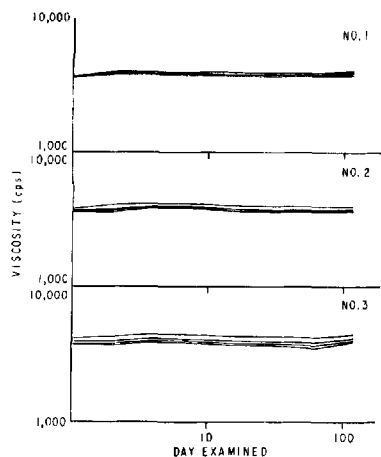
Fig. 1.—The effects of age on the viscosities of ammonia emulsions (logarithmic scale). Samples 1, 2, and 3 represent ammonia concentrations of 0.6, 2, and 6 mg./100 ml., respectively.
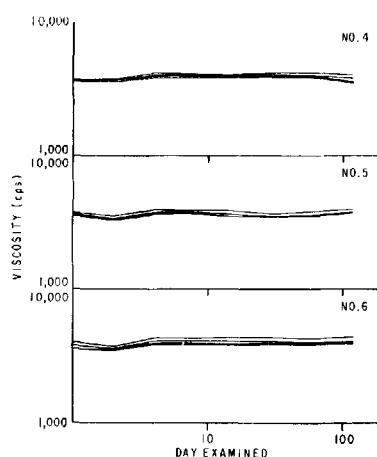

Fig. 2.—The effects of age on the viscosities of AMP emulsions (logarithmic scale). Samples 4, 5, and 6 represent AMP concentrations of 2, 6, and 20 mg./100 ml., respectively.

The fact that samples 2 and 5 both showed a smaller mean droplet size and droplet distribution than was seen with samples 1 and 4, respectively, infers a greater degree of stability between the emulsions as the amine concentration was increased. Even though a droplet size could not be calculated in either sample 3 or 6, the fact that both samples had sizes completely below 0.5 μ can have significant implications as to their stability.

Several published reports have shown the importance and usefulness of time plots on a logarithmic scale (33–36) in stability studies on dispersed systems. These studies demonstrated that linear relations existed when the logarithm of some property to be followed in the system was graphed with the logarithm of time. For example, Wood and Catacalos (36) applied this concept to studies on viscosity and concluded that changes in viscosity expected to occur after 1 year can be predicted from data on only 100 days.

In order to perform a similar evaluation of the data obtained in this study, logarithm time plots of viscosity and age for the various ammonia emulsions and AMP emulsions were prepared and are represented in Figs. 1 and 2, respectively. Figure 1 shows a fairly linear relation for each sample. Sample 3 takes a slight rise between day 60 and day 120. However, this increase, if continued, would not result in an appreciable rise after 1 year. Figure 2 also shows fairly good linearity. Therefore, no appreciable viscosity change should be seen after 1 year.

SUMMARY

Six olive oil-in-glycerin emulsions were prepared wherein ammonia and 2-amino-2-methyl-1,3-propanediol (AMP), in various concentrations, served as saponifying agents. Six-tenths, 2, and 6 mg. ammonia/100 ml. and 2, 6, and 20 mg. AMP/100 ml. were used in making the emulsions. The emulsions were stored at room temperature (25°) and droplet size, rheology, and emulsion stability studied on days 1, 2, 4, 7, 14, 30, and 60. Day 1

corresponded to the day the emulsions were prepared.

Droplet size, as measured from photographs taken by phase contrast photomicrography, was inversely related to amine concentration. This work also demonstrated that a droplet size frequency analysis was much more meaningful to a stability study than was mean droplet size data alone.

Rheology was studied on the respective test days with a Brookfield LVT viscometer. Viscosity was calculated from Brookfield data using the "n value" method described by Runikis and co-workers. These studies revealed the existence of non-Newtonian pseudoviscous flow with occasional thixotropy.

Logarithmic graphs of viscosity and time illustrate stability in the emulsion systems. These graphs also suggest that no significant changes in viscosity would be expected over longer time periods.

REFERENCES

(1) Sherman, P., *J. Pharm. Pharmacol.*, **16**, 1(1964).
(2) van den Tempel, M., "Second International Congress of Surface Activity," vol. I, Schulman, J. H., ed., Butterworth Scientific Publications, London, England, 1957.
(3) Lloyd, N. E., *J. Colloid Sci.*, **14**, 441(1959).
(4) Richardson, E. G., *ibid.*, **5**, 404(1950).
(5) *Ibid.*, **8**, 367(1953).
(6) Mullins, J. D., and Becker, C. H., *J. Am. Pharm. Assoc., Sci. Ed.*, **45**, 105(1956).
(7) *Ibid.*, **45**, 110(1956).
(8) Knoechel, E. L., and Wurster, D. E., *ibid.*, **48**, 1(1959).
(9) Rowe, E. L., *J. Pharm. Sci.*, **54**, 260(1965).
(10) Sumner, C. G., "The Theory of Emulsions and Their Technical Treatment," The Blakiston Co., New York, N. Y., 1954.
(11) Lyttleton, D. U., and Traxler, R. N., *Ind. Eng. Chem.*, **40**, 2115(1948).
(12) Sherman, P., *Research (London)*, **8**, 396(1955).
(13) Sherman, P., *Proc. Third Intern. Congr. Surface Activity*, **2**, 596(1960).
(14) Sherman, P., *Food Technol.*, **15**, 394(1961).
(15) Michaels, A. S., and Bolger, J. C., *Ind. Eng. Chem. Fundamentals*, **1**, 24(1962).
(16) *Ibid.*, **1**, 153(1962).
(17) de Vries, A. J., "Rheology of Emulsions," Sherman, P., ed., Pergamon Press, New York, N. Y., 1963.
(18) van den Tempel, M., *ibid.*
(19) Albers, W., and Overbeck, J. T. G., *J. Colloid Sci.*, **14**, 501(1959).
(20) *Ibid.*, **14**, 510(1959).
(21) *Ibid.*, **15**, 489(1960).

(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 Catacalos, 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