Comparison of Ultracentrifugal Stability Parameters with Long-Term Shelf Stability of Emulsions

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ABSTRACT AND SUMMARY

The validity of prediction of shelf stability from ultracentrifugal parameters determined on newly prepared Nujol-in-water emulsions stabilized with sodium dodecylsulfate (0.2 to 0.4%), cetylpyridiniumchloride (0.1 to 0.2%), Triton X-100 (0.08 to 0.4%), or Tween 20 (0.08 to 0.4%) was tested by allowing samples to age for periods up to 3 yr. They were then reexamined visually, and an empirical rating scheme devised for describing their stability semiquantitatively. In some cases it was also possible to redetermine the ultracentrifugal parameters on the aged emulsions. None of the ultracentrifugal parameters of the fresh emulsions predicted the order of actual shelf stability correctly in all cases. Possible reasons for the discrepancies are discussed.

INTRODUCTION

Ever since the early ultracentrifugal study of emulsions (1-3) the important practical question has been raised as to whether the results of such quick and relatively easily made measurements on freshly prepared emulsions can be used with confidence to predict longterm storage stability. By stability in this paper is meant resistance to coalescence (separation of oil) rather than any less drastic change such as simple creaming (4,5). As early as a discussion of possible practical applicability following initial presentation of the ultracentrifugal method (3), some of the possible reasons why such a correlation might not exist were already pointed out. Garrett (1), however, concluded that the analytical ultracentrifuge is an excellent tool for the evaluation of emulsion stability, although he may have been referring to creaming rather than coalescence. Sherman (6), on the other hand, suggests that in all likelihood none of the accelerated tests for evaluating emulsion stability, including ultracentrifugation, are likely to be reliable since all proceed under different conditions than does normal aging, and that such results can not be relied on unless an empirical relation can be established with instability under normal storage conditions.

In order to provide a definitive answer to this question, a selection of emulsions on which the rate of separation of oil and quantity separated after various periods of ultracentrifugation had been determined (1,7,8-9) were allowed to stand undisturbed for periods up to 3 yr, and then evaluated visually for shelf stability. In addition, many of these samples were rerun in the ultracentrifuge after this time, and the parameters so determined compared with the original values. The results obtained show that ultracentrifugal separation of oil from oil-water (O-W) emulsions, despite its great value in elucidating the detailed mechanism of many of the steps in the demulsification process, can not be used safely to predict shelf stability.

EXPERIMENTAL PROCEDURES

The sodium dodecylsulfate (SDS), Triton X-100, Tween 20, cetylpyridiniumchloride (CPyCl) and Nujol used were characterized in a previous publication (8). Emulsions were prepared as described previously (1,7,10) by initial mixing of oil and an aqueous solution of the emulsifier in a counter-rotating mixer, followed by repeated passes thru a mechanized hand homogenizer (see footnote a, Table II). Additional small amounts of water or concentrated emulsifier solution were added with minimum agitation to portions of the master batch so as to obtain a series of emulsions all of the same phase volume ratio and drop size distribution but with varying concentration of emulsifier. The quantities of oil and water are expressed in volume %, and emulsifier concentration as % based on grams of emulsifier per mililiter of aqueous phase. After withdrawal of small amounts of emulsion for the initial ultracentrifugal studies the residual emulsion (ca. 49 ml.) was stored in 125 ml Erlenmeyer flasks, carefully closed to prevent any evaporation, allowed to stand undisturbed in an air-conditioned building at room temperature (ca. 22-26 C) for 1-3 yr, and examined visually at intervals as to the state of preservation of the emulsion.

In an attempt to quantify these observations a numerical rating scale was developed based on the quantity of visible oil present in the emulsion as given in Table I. On this scale the most stable emulsions are given the number 1, corresponding to no visibly apparent separation of oil, and the least stable the number 6, corresponding to the presence of

TABLE I

Definition of Visual Stability Scale[a]

Shelf stability number	Characteristics of the aged emulsion
1	Homogeneous cream layer throughout the container. No visible separated oil layer. No oil visible at the emulsion/air interface.
2	Homogeneous cream layer throughout the container. Minute, barely observable oil droplets or slicks at the air/emulsion interface, which redisperse on tilting the tube.
3	Homogeneous cream layer throughout the container. Very small oil droplets at the air/emulsion interface, which redisperse easily on rocking the container (no shaking necessary).
4	Homogeneous cream layer throughout the container. Separated oil present as large, small, and minute oil droplets or patches covering about 25 to 50% of the emulsion/air interface. Oil redisperses easily on inverting the container two or three times.
5	Homogeneous cream layer throughout the container. Very thin continuous oil film present, covering 50 to 100% of the emulsion/air interface.
6	Distinct oil layer present at the emulsion/air interface. Oil drops also visible within the residual cream layer.

[a] With the exception of emulsions of stability number 6, in which extensive irreversible coalescence has occurred, the small amounts of separated oil were as readily redispersed in the cream layer as was the water which had separated on standing.

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TABLE II

Shelf Stability Numbers of Aged 50% Nujol -50% Water Emulsions[a] Based on Visual Observations

Emulsion number	Conc. of emulsifier, % on aq. phase	Age after formulation, days	Shelf stability number
Sodium Dodecylsulfate			
M111968	0.2	903	4
M062769-1	0.2	1048	4
A032572N8-2	0.2	46	4
A020872N8-2	0.2	92	4
A120371N8-2	0.2	159	3
A111271N8-2	0.2	180	4
A041972N13-2[b]	0.2	21	2
A050471N-2.2	0.22	372	4
M062769-5	0.4	1048	1
Triton X-100			
M111969TR-0.8	0.08	903	6
M111969TR-1.0	0.1	903	5
M111969TR-1.2	0.12	903	4
A052670TR-1.2	0.12	715	4
M111969TR-1.5	0.15	903	1
A052670TR-1.5	0.15	715	3
M111969TR-1.8	0.18	903	2
A090969-2	0.2	974	3
M111969TR-2	0.2	903	2
A052670TR-2	0.2	715	1
A090969	0.25	974	2
A052670TR-2.5	0.25	715	1
A052670TR-3.0	0.3	715	1
A052670-TR-3.5	0.35	715	1
A052670TR-4	0.4	715	1
Tween 20			
All these emulsions (Tween concentrations 0.08, 0.10, 0.12, 0.15, 0.18, 0.20, and 0.40%) had separated large quantities of bulk oil after 903 days, so all had a shelf stability number of 6.			
Cetylpyridinium Chloride			
M111869C	0.2	904	4

[a] Several of these emulsions are the identical preparations described by Vold and Mittal (references 7 and 8) and may be identified by their numbers. Complete details of preparation are given in the cited papers. This involved preparation of a stock emulsion by mixing specified constant volumes of oil and water at 5000 rpm for 5 min in a Brookfield counter-rotating mixer, followed by eight passes through a motorized Cenco hand homogenizer, and subsequent adjustment of the concentration of the emulsifier and the phase volume ratio.

[b] This emulsion was passed through the homogenizer thirteen rather than the standard eight times.

a layer of separated oil at the top, and visible drops of oil within the residual cream layer. Despite the subjectivity of such a visual rating system, it is reassuring that independent observation of the emulsions by two different observers frequently resulted in assignment of the same "shelf stability number," and in no case was there ever a difference of more than one.

There was a special problem with ultracentrifugation of these aged emulsions in addition to the difficulties inherent in the general method, which resulted in somewhat greater scatter of the data points than in much of the previously reported work. Where some oil had separated on standing, it was difficult to withdraw an 0.8 ml representative sample of residual emulsion through the syringe without also including small but variable numbers of separated oil droplets even though those had been blended into the residual emulsion. These appear as free oil much more rapidly in the ultracentrifugal field than does oil resulting from coalescence of emulsified oil, giving rise to greater variability in the numbers reported for total amount of oil separated after a given interval (particularly at "zero time") than in the case of data obtained on unaged samples. However, outside this complication the results obtained were of about the same precision as in the earlier work.

Ultracentrifugation of the aged emulsions was carried out at 39,460 rpm at 25 C as in previous studies (3,11), which provided data on the amount of separated oil and its rate of separation as a function of time in the ultracentrifugal field. The data were also tested for compliance with conventional kinetic rate expressions (9.10) in an attempt to determine specific rate constants of demulsification wherever possible.

RESULTS

Table II gives the actual observed relative stability of 50% Nujol-50% water emulsions stabilized with various concentrations of SDS, Trition X-100, Tween 20, or CPyCl after standing undisturbed for extended periods. Comparison of these results with the ultracentrifugal parameters determined on the freshly prepared emulsions is the best criterion of the ability of the latter to predict shelf stability. It is interesting to note that the shelf stability of the Triton emulsions began to decrease when the concentration of Triton was less than 0.15%.

In Table III are assembled ultracentrifugal data on these identical emulsions (or very similar ones) shortly after preparation, taken from previous publications. The relative order of the shelf stability numbers of the various emulsions can be compared to the relative stability order based on the ultracentrifugal parameters of the fresh emulsions.

Ultracentrifugal studies were also made of the aged emulsions where possible in order to determine whether there had been any quantitative change in the mode of oil separation in the ultracentrifugal field as a result of the aging. No experiments of this type were possible on the emulsions stabilized with Tween 20 since all had broken so badly that adequate sampling was impossible. Typical results obtained on aged Nujol-in-water emulsions stabilized

TABLE III

Comparison of Relative Stability from Ultracentrifugal Parameters on Fresh Emulsions[a] with Actual Shelf Stability

Emulsion number	Emulsifier	Shelf stability number[b]	% Oil sep. in UC after		Rate of oil sep. (%/min.) in UC after		Half life in UC (min.)	Parameters of the empirical equation[c]	
			25 min.	75 min.	25 min.	75 min.		a,%	$bx10^2$, min^{-1}
A090969	0.15% Triton	1	10.8	15.8	0.11	0.08	541	–	–
123 and 133C	0.4% SDS	1[d]	4.5	11.6	0.16	0.16	3.05×10^4[e]	–	–
A090969	0.2% Triton	2	4.2	8.1	0.09	0.047	1003	–	–
M111968	0.2% SDS	4	23.6	42.8	0.53	0.53	56	91.6	–
A112669	0.1% CPyCl	4[f]	17.5	27.4	0.24	0.16	282	–	–
A091069	0.2% Tween	6	21.9	26.1	0.21	0.033	699	29.5	13
M111969TW	0.15% Tween[g]	6	8.3	11.8	0.15	0.04	–	15.4	4.6
A091069	0.15% Tween[g]	6	29.4	33.8	0.25	0.038	558	37.8	14.8

[a] Ultracentrifugal data on all these emulsions except those with 0.4% SDS can be found in references (7) and (8). Data on the 0.4% SDS emulsions are from references (3) and (9).

[b] See Tables I and II. Values listed were determined after 2 to 3 yr undisturbed standing on the shelf. The stability decreases from 1 to 6, 1 signifying a completely stable emulsion (to visual examination) and 6 a badly broken emulsion.

[c] Vold and Mittal (9) showed that in some cases, separation of oil from an emulsion in the ultracentrifuge could be represented by the equation: $t/x = 1/ab + t/a$, where x is the percent oil separated at time 5, a is the extrapolated maximum amount of oil which would have separated after infinite time, and b is an empirical constant.

[d] Based on observation of a similarly prepared emulsion, M062769-5.

[e] The specific reaction rate constant for this system was obtained using emulsion H043073 (9).

[f] Based on observation of a similarly prepared emulsion M111869C, but in which the concentration of CPyCl had been adjusted to 0.2%.

[g] Obviously, much better initial emulsification was achieved with one of these stock preparations than with the other.

with 0.2% SDS are shown in Figure 1, in which the data are plotted in a form in which they would give a linear relation with time dependent on whether the separation of oil is occurring according to an over-all zero, first, or second order process, or according to an empirical relation previously found (7,11) to represent the behavior of certain freshly prepared emulsions. Here only the plot of t/% oil vs. t is linear, corresponding to a fit of the data to the empirical equation. Results on fresh emulsions with which these can be compared have already been reported (3,7-10).

Figure 2 shows the results obtained with freshly prepared and aged Nujol-in-water emulsions stabilized with 0.4% SDS. In this instance the ultracentrifugal stability has apparently increased with age, the older emulsion having a longer induction period before the separation of any oil, and then separating oil more slowly than in the case of the fresh emulsion. The data on the fresh emulsion resemble those obtained using 0.4% SDS in previous work (3,9) except for the existence of an induction period in the present case. The data in this case are indicative of a zero order reaction.

Data illustrative of the results obtained with aged Triton-stabilized Nujol-in-water emulsions are shown in Figure 3. Here, although a straight line of sorts might be drawn through the points giving percent oil separated against time, as was usually done in the earlier work, a much better linear relation is found when the data are plotted according to the empirical equation (7). However, as is reported in Table IV, different functional relationships between percent oil separated and time were found with aged emulsions which had been stabilized with different concentrations of Triton. For comparative purposes, data on ultracentrifugal expression of Nujol from fresh emulsions stabilized with 0.08 to 0.25% Triton can be found in Figure 2 of reference 7, Figure 5 of reference 8, Figure 5 of reference 9, and in greater detail in Mittal's dissertation (12).

The important results of these ultracentrifugal determinations are summarized in Table IV. In all cases the data for oil separation in the ultracentrifuge of both the fresh and the aged emulsions studied were plotted, as in Figure 1, to determine which functional relationship best fitted the experimental data. Specific rate constants for the demulsification reaction were calculated from the slopes of the lines where a linear relation was found with time. Since the amount of oil separating rapidly at the beginning of ultracentrifugation prior to establishment of a steady state is also of interest, this quantity is also tabulated, together with the extrapolated value found by extrapolation of the relatively linear portion of the % oil separated-time curve to zero time. To facilitate comparison of kinetic parameters with the actual long term stability of the emulsion the shelf stability numbers are also given.

DISCUSSION

Prior to this work, as stated in the introduction, there had been much speculation in the literature as to whether ultracentrifugal parameters determined on newly prepared emulsions could be used to predict the shelf stability of the emulsion, and so provide a rapid means of testing the efficacy of different emulsifying agents. Unfortunately, although such studies have been of considerable value in understanding the nature of the demulsification process and the reasons for the effectiveness of certain emulsifiers and additives (10,11,13), the present data show conclusively that none of the ultracentrifugal parameters determined on fresh emulsions can be used with confidence for predicting long term stability.

In Table III the emulsions are arranged in order of decreasing stability as judged by their appearance after standing undisturbed for long period. On this basis, which ap-

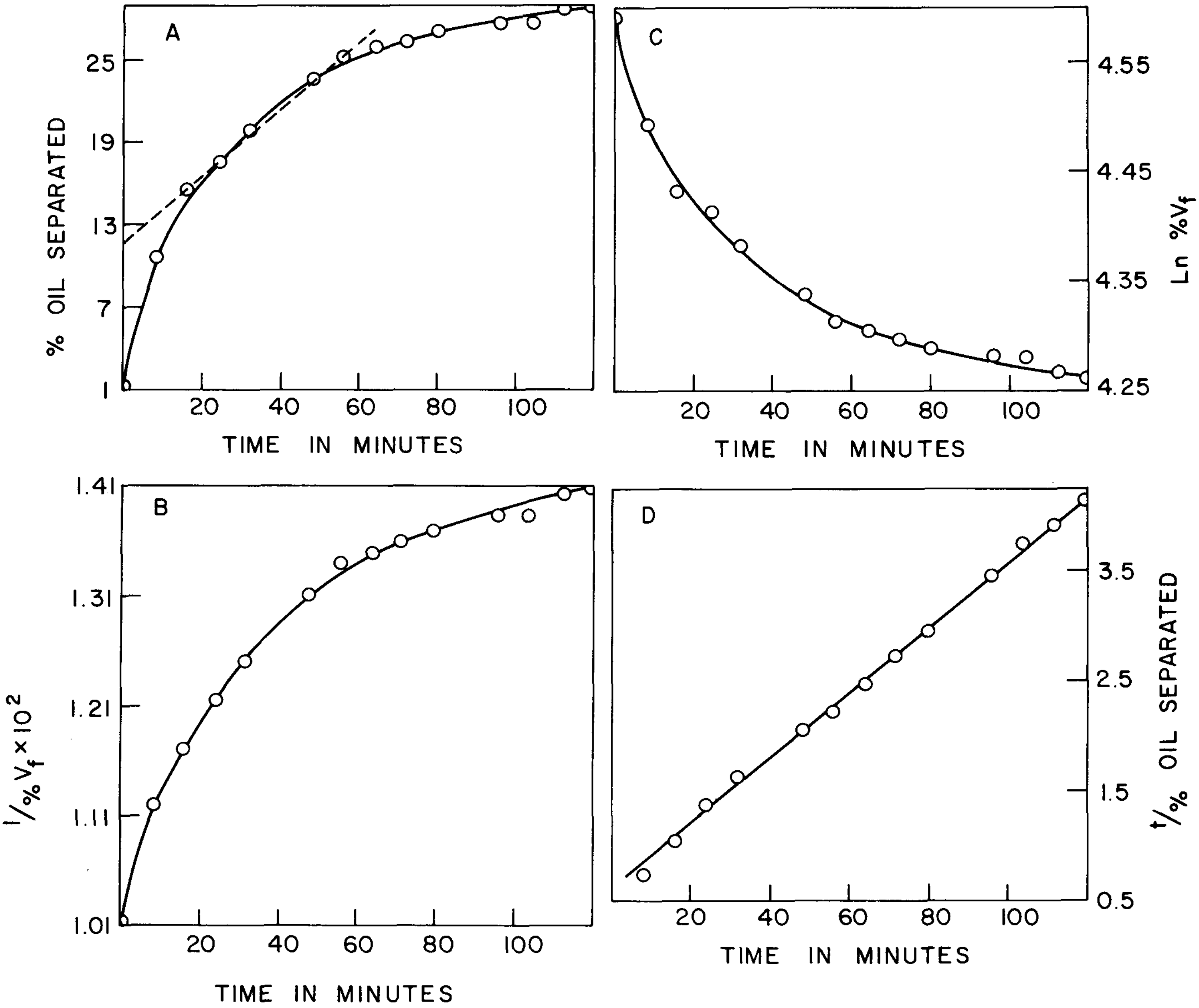

FIG. 1. Ultracentrifugal separation of oil from a 50% Nujol-50% water-0.2% sodium dodecylsulfate emulsion aged 1229 days. A. This plot would be linear if the separation of oil were a zero order process. B. This plot would be linear if the separation of oil were a second order process. C. This plot would be linear if the separation of oil were a first order process. D. The linearity of this plot shows that the separation of oil follows the empirical equation of Vold and Mittal. % V_f is the percent of the original volume of emulsion still present at time t.

proximates most closely to shelf stability, they divide into three groups. Those stabilized with 0.15% or 0.2% Triton X100 or 0.4% SDS were extremely stable; those with 0.2% SDS or 0.1% CPyCl were of intermediate stability, while those with 0.15 or 0.2% Tween 20 were completely unstable. If the quantity of oil separated after an arbitrarily chosen 25 min. of centrifugation of the fresh emulsions is selected as a criterion of stability, 0.4% SDS and 0.2% Triton-stabilized emulsions would be picked as the best, in accord with the experimental observations, but the 0.15% Tween emulsion, which had broken compeltely, would be rated nearly as good. The 0.2% SDS emulsion, which was only partially broken after nearly 3 yr, would be rated as one of the worst. Similar difficulties are experienced if the rate of separation of oil after 25 min is used as the measure of stability. On this basis, 0.2% Tween, 0.15% Triton, and 0.4% SDS would be picked as very good, and 0.2% SDS as the worst of the lot. Here again, although the emulsions which actually were most stable would have been so rated by this criterion, one of the least stable would have been so rated by this criterion, one of the least stable would have been included in the superior group while one which turned out to be better than any of the Tween-stabilized emulsions would have been rated as worst. A further difficulty with these criteria is the inversions in the order of relative stability which occur if a different period of centrifugation is chosen for comparison of the results with the different emulsions.

Similar lack of concordance between the actual longterm stability results and the predictions from ultracentrifugal data on the fresh emulsions is also found with the other suggested parameters. The half life of the process can be calculated by standard means (14) from the specific reaction rate constant. Using this criterion, emulsions with 0.4% SDS or 0.2% Triton would be expected to be the most stable (longest half-lives) in agreement with observation. However, the Tween-stabilized emulsions, which had broken, would have been rated as more promising than the 0.15% Triton emulsion, which actually turned out to be one of the most stable. Use of the parameters of the empirical equation, which is limited in any event to emulsions in which it adequately represents the data, is equally unsatisfactory. Thus, on the basis of the parameter a, the unstable 0.15% Tween emulsion is apparently much better

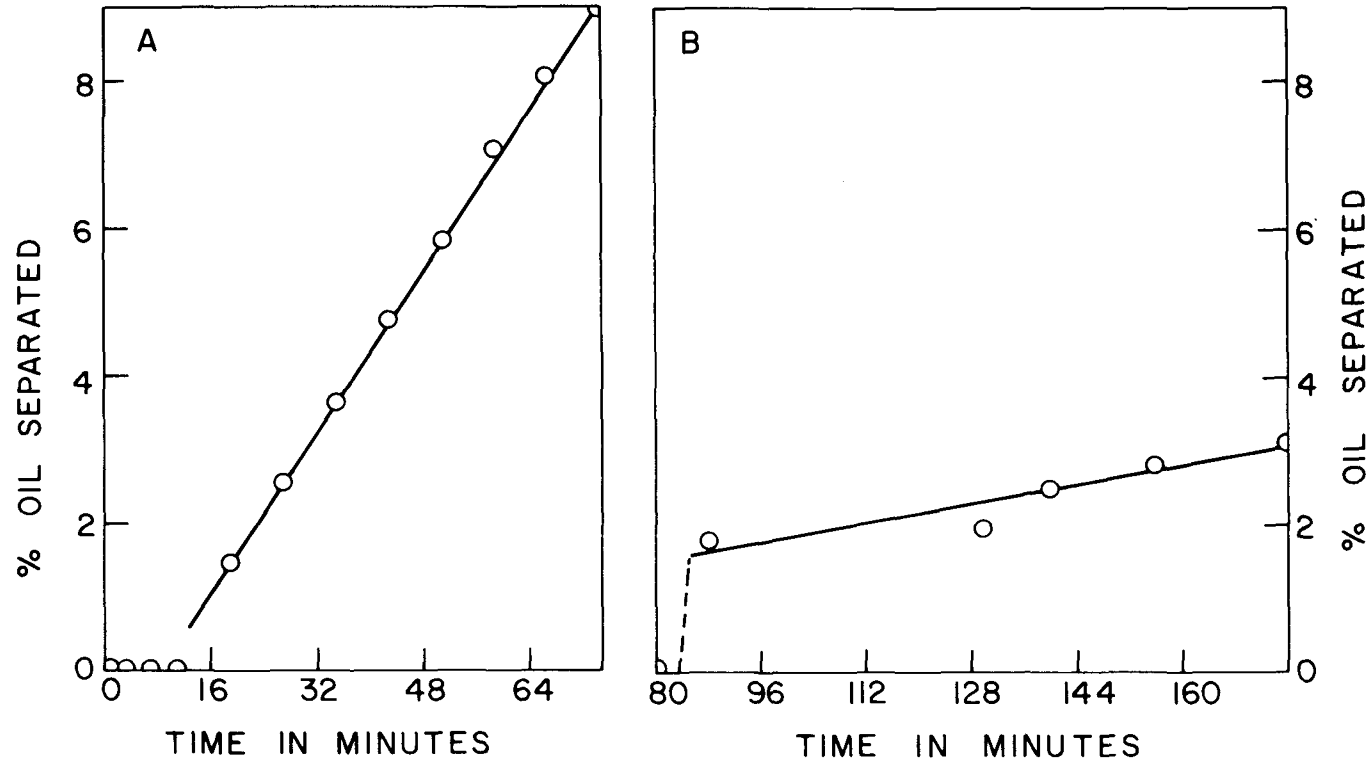

FIG. 2. Ultracentrifugal separation of oil from a 50% Nujol-50% water-0.4% sodium dodecylsulfate emulsion. A. Aged 2 days. B. Aged 1230 days. In this case, no free oil appeared until after 80 min centrifugation at 39,460 rpm.

TABLE IV

Ultracentrifugal Parameters of Fresh and Aged 50% Nujol – 50% Water Emulsions

Emulsifier	Age in days	Shelf stability number	% Oil sep. at zero time		% Oil sep. at 25 min.	Kinetic order of oil separation	Specific rate constant
			Extrapolated	Actual			
0.2% SDS	2	–	6.8	0(?)	23.6	1	7.71×10^{-3} min^{-1}
	1229	4	11.4	1.0	17.8	empirical eq.[a]	–
0.4% SDS[b]	2	–	0	0	2.6	0	0.135%[c] min^{-1}
	1230	1	0	0	0	0[d]	0.018%[c] min^{-1}
0.1% Triton	2	–	5.7	5.0	11.1	1	2.0×10^{-3} min^{-1}
	1092	5	32.2	21.8	34.9	1[e]	1.6×10^{-3} min^{-1}
0.12% Triton	2	–	4.8	0(?)	7.5	1[f]	1.1×10^{-3} min^{-1}
	1094	4	18.7	6.4	20.2	empirical eq.	–
0.2% Triton	2	–	1.2	0.4	4.2	1	7.1×10^{-4} min^{-1}
	1000	2	27.8	14.0	28.2	indeterminate[g]	–

[a] According to this equation, $t/x = 1/ab + t/a$, where x is the percent oil separated after t min, a the extrapolated maximum amount of oil separated after infinite time, and b an empirical constant.

[b] All results reported here were obtained using stock emulsion M062769-5.

[c] These results cannot be expressed in the preferable units of mm^3 oil separated per minute because of lack of information on the exact volume of emulsion in the ultracentrifuge cell.

[d] There was no separation of oil during the first 80 min of centrifugation.

[e] After the first 8 min.

[f] *After the first 7 min.*

[g] This emulsion underwent more rapid separation of oil during the first 32 min than is reconcilable with any of the standard rate laws. After this, it gave nearly linear plots following the linear form of zero, first or second order expressions equally well for the next 132 min. Apparent rate constants calculated from these lines are: zero order, 0.061% min^{-1}; first order, 9.2×10^{-4} min^{-1}; second order, 1.4×10^{-5}%$^{-1}$min^{-1}. The empirical equation is fitted exactly for the first 88 min with a = 35.09% and b = 0.178 min^{-1}, but systematic deviation occurred after longer periods of centrifugation.

than the 0.2% SDS emulsion of intermediate stability.

One of the reasons for these failures of the ultracentrifugal parameters to predict correctly the relative order of practical stability is evident from the results summarized in Table IV. If the results on the fresh emulsions are to be successful in predicting long term storage stability, there must not be any change in the nature of the process of oil separation over the time interval involved. Thus, if the specific rate constant for separation of oil is used as the criterion, the order of reaction must not change with the age of the emulsion. It is clear that changes in the way in which oil separates from the emulsion occur during aging, as indicated by the changes found in the kinetic order of the reaction on the fresh and the aged emulsions. Hence, predictions of shelf stability based on the rate constants of the fresh emulsions (as the equivalent half lives) are bound to fail, since at some point in time during storage, the emulsion has changed in such a way that the initial rate equation no longer fits the data.

Actually, this conclusion might have been anticipated

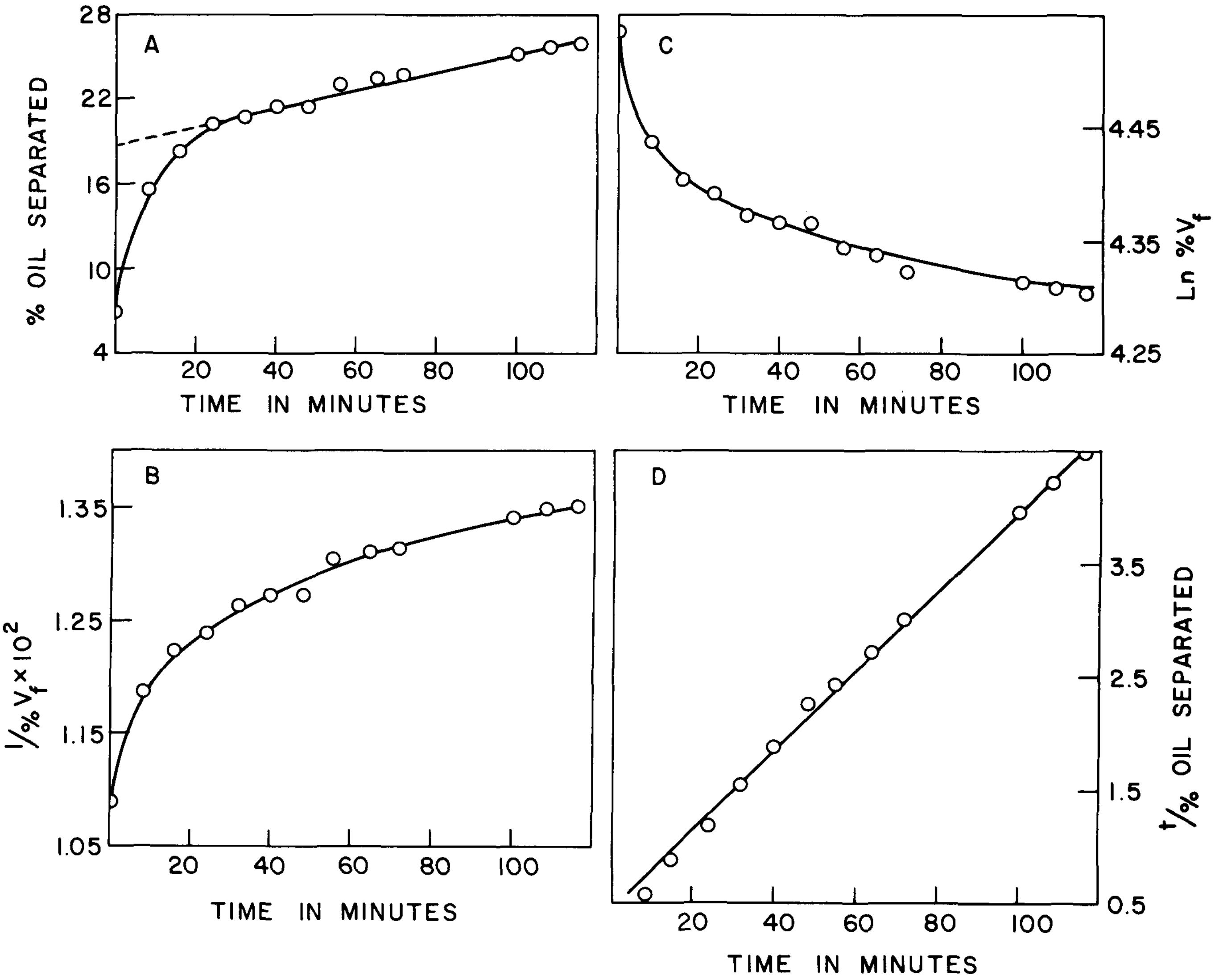

Fig. 3. Ultracentrifugal separation of oil from a 50% Nujol-50% water-0.12% Triton X-100 emulsion aged 1094 days. The nonlinearity of the plots of 3A, 3B, and 3C shows that separation of oil is not occurring according to zero, second, or first order rate expressions. The linearity of 3D shows that the results accord with the empirical equation of Vold and Mittal. %V_f is the percent of the original volume of emulsion still present at time 5.

from certain observations already in the literature, although hitherto there were no suitable results on long term shelf stability with which the ultracentrifugal data could be compared. It was earlier shown (4) that in Nujol-water-SDS systems the rate of separation of oil was not a constant, but underwent qualitative changes dependent on the amount which had already separated, and varied with the age of the emulsion (15). It was also reported (16) that in toluene-water-polyoxyethylene-30-stearate emulsions the kinetic order of the rate of separation of oil changed from one to zero as the percent oil separated changed. Equally significantly, Boyd et al. (17) found that the creep compliance of Nujol-water emulsions stabilized with mixtures of Tweens and Spans underwent changes with the age of the emulsion. This is the measurement from which surface elasticity and surface viscosity can be inferred, and these were shown to be determinative of the rate of coalescence in these emulsions. In view of all these observations, a thoughtful reader should have become very skeptical of the ability of any tests on newly prepared emulsions to predict their longterm stability.

Actually, considering the differences in the physical conditions, it is surprising that the ultracentrifugal parameters agree with the shelf stability in as many cases as they do. In the ultracentrifuge, the originally spherical oil drops are flocculated and distorted into polyhedra in a foam-like structure from which residual water drains out under the pressure of the centrifugal force field from the flattened aqueous lamellae between the oil drops, and through the larger channels in the Plateau borders where these meet. Subsequently, rupture of the adsorbed film of emulsifier must take place before coalescence can occur, and a detectable layer of free oil appears in the ultracentigue cell. In the case of a normal emulsion standing on the shelf, the rate of flocculation, i.e., the rate at which drops collide and form aggregates, may also be important, as well as the rate of coalescence, and in the gravitational force field the coalescing drops approach each other essentially as spheres. Although the same basic properties of the surfaces, such as extent of coverage with adsorbed emulsifier, rheological characteristics of the adsorbed film, rate of drainage of the continuous aqueous phase through small channels, etc., are involved in both situations, the differences in conditions apparently result in changes in the relative importance of the individual steps in the overall process of separation of oil in the two cases, making sure prediction of the one from results on the other impossible.

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[Received September 30, 1976]

ERRATUM

In "Applications of Pulsed NMR to Fatty Emulsions" by J. Trumbetas, J.A. Fioriti, and R.J. Sims, [*JAOCS* 53:722 (1976)], on page 725 there is an expression for percent interaction which reads

$$\frac{45.5 \times 100}{38.8} - 100 = 7.0 \text{ (at 25 C)}$$

This should read

$$\frac{41.5 \times 100}{38.8} - 100 = 7.0 \text{ (at 25 C)}$$

The number 45.5 should read 41.5.