

Stability of Nonaqueous Emulsions

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We examined the stability of emulsions of oil in several nonaqueous polar liquids using commercially available nonionic surfactants. Stable nonaqueous emulsions were only obtained with formamide and dimethylsulfoxide. Hydrogen bonding, and not polarity, appears to be the important factor determining the emulsifying power of a solvent. Ostwald ripening plays a much more important role in the stability of these nonaqueous emulsions than in the corresponding aqueous systems. This destabilizing process can be prevented, however, by addition to the oil phase of a small amount (1%) of an oil that has a very low solubility in the continuous phase. Furthermore, a larger size of the surfactant molecule protects emulsions against droplet coalescence. Thus, emulsions in formamide and dimethylsulfoxide did not show any breakdown when stabilized with a triblock copolymer of polyoxyethylene-polyoxypropylene-polyoxyethylene. © 1997 Academic Press

Key Words: emulsions; Ostwald ripening; surfactants.

INTRODUCTION

An emulsion is a system in which one fluid is dispersed in another with which it is immiscible. Macroscopic separation of the phases is prevented by the addition of a suitable surfactant. In the vast majority of emulsion research one of the liquids has been water. Nonaqueous emulsions, however, could replace regular aqueous emulsions wherever the presence of water is undesirable; for example, in cleaning systems that are sensitive to formation of rust such as engines and other mechanical systems, or for doing sol-gel processes with hydrolyzable metal alkoxides in organized media in a controlled way. Only occasional reports on nonaqueous emulsions have appeared (1–3).

Two strategies can be considered when searching for stable nonaqueous emulsions. One of these is to design surfactants which have two incompatible blocks, each of which is soluble selectively in one of two selected immiscible liquids. In this way diblock copolymers of polystyrene and polyisoprene were able to stabilize DMF/hexane emulsions for almost 24 h (1). The other approach is to find suitable oil-immiscible polar liquids that can replace water using existing surfactants (which have been designed to work well with water). Thus, nonionic surfactants with HLB numbers (hydrophilic-lipophilic balance) around 12 were found to stabi-

lize oil-in-formamide emulsions (2, 3). The first approach has the drawback of necessitating the specific design and characterization of a new surfactant for each combination of liquids. In this work we therefore chose the second approach.

A liquid capable of replacing water in an emulsion should have a high polarity to make it immiscible with oils and to make it a good solvent for the hydrophilic part of surfactant molecules. Furthermore, hydrogen bonding is expected to play a role in solvating both ionic and nonionic surfactants and in the formation of a hydrogen-bonded network in the liquid itself. The influence of these factors is investigated in this work by examining emulsion stability for a variety of polar liquids in combination with surfactants over a range of HLB numbers.

The composition and type of the oil is shown to play an important role as well. It will be shown that Ostwald ripening plays an even more important role in nonaqueous emulsions than in aqueous emulsions. Using the insights gained we were able to make high internal phase oil-in-polar-liquid emulsions that are stable indefinitely.

EXPERIMENTAL

Materials

Polar solvents were water (deionized), formamide (FA, Aldrich 99.5+%), *N*-methylformamide (NMF, Aldrich 99%), *N,N'*-dimethylformamide (DMF, Fisher, A.C.S. reagent), dimethylsulfoxide (DMSO, Fisher, A.C.S. reagent), methanol (Fisher, A.C.S. reagent), and acetonitrile (Fisher, A.C.S. reagent). Oils used were decane (Aldrich, 99+%) and silicone oil (Fisher, boiling point >200°C, density determined at 0.959 g/ml).

The nonionic surfactants were all obtained from Aldrich. The polyoxyethylene alkyls are designated by A-*n*, where *n* is the (average) number of oxyethylene units in the chain: Brij 52 (*n* = 2, HLB = 5.3), Igepal CO-520 (*n* = 5, HLB = 10.5), Triton X-100 (*n* = 10, HLB = 13.6), Brij 35 (*n* = 23, HLB = 16.9), Igepal CO-890 (*n* = 40, HLB = 17.9), and Igepal CO-990 (*n* = 100, HLB = 19.1). The triblock copolymer surfactants polyoxyethylene-polyoxypropylene-polyoxyethylene differed in their (number averaged) molecular mass M_n and their polyoxyethylene content (%)

EO as a fraction of the molecular mass by weight). They will be designated as $EaPbEa$, where $2a$ is the number of oxyethylene units (E) and b is the number of oxypropylene units (P). HLB numbers were assigned to them in the usual way, by dividing the weight percentage EO by 5 (4). The surfactants used were E3P43E3 ($M_n = 2800$, 10% EO, HLB = 2), E20P70E20 ($M_n = 5800$, 30% EO, HLB = 6), and E76P29E76 ($M_n = 8400$, 80% EO, HLB = 16). All surfactants were soluble in the polar liquids and insoluble in decane, with the exception of Brij 52, which was soluble only in the oil.

Methods

For the stability tests emulsions were prepared by placing 2.0 g of an 18.3 wt% solution of surfactant in polar solvent in a tall 8-ml vial and adding 2.0 ml of decane. This corresponds to an oil volume fraction of approximately 50%. The vial was then vigorously shaken by hand until a very viscous emulsion formed and was allowed to rest at a temperature of $21 \pm 0.5^\circ\text{C}$. The behavior of the emulsions was followed over time by noting the amount of creaming and breaking. The stability criterion used was the "time until breaking," i.e., the time after which 5% of the total amount of oil was floating on the emulsion. All emulsions were tested at least twice in this way. The time until breaking was reproducible to about 20%. Some emulsions were prepared by passing the hand-shaken emulsions through a porous membrane (MSI, nylon, $0.45 \mu\text{m}$ pores) using a syringe. This generally led to smaller droplets but did not have a large effect on the time until breaking.

Droplet size distributions were determined using an optical microscope (Nikon MicroPhot-FX) and a digital camera. Emulsions used for these experiments were filtered through a membrane (nylon, $0.45 \mu\text{m}$) in order to obtain a reproducible initial size distribution with small droplets. Samples were taken after specified times and diluted with the continuous phase by gentle stirring. In each population about 300–400 droplets were sized and a histogram of their diameters was made with $0.5 \mu\text{m}$ bins.

RESULTS & DISCUSSION

In our search for solvents that can replace water to give nonaqueous emulsions we were led by considerations of the polarity and hydrogen bonding abilities. Related physical parameters are the dipole moment (μ), relative permittivity (ϵ), and Hildebrand cohesive energy density (δ_H^2), which are given in Table 1 for the solvents used. The Kamlet–Taft solvatochromic parameters α , β , and π^* are also shown (5). They are normalized numbers for the neat solvent that express respectively the hydrogen bond donating ability, the hydrogen bond accepting ability, and a combination of polarity and polarizability. All solvents shown have high, though

TABLE 1
Physical Parameters and Kamlet–Taft Parameters
of the Polar Solvents Used

	$\mu(\text{D})$	ϵ	δ_H^2	α	β	π^*
Water	1.85	80	549	1.17	0.18	1.09
FA	3.73	110	362	0.71	0.60	0.97
NMF	3.83	184	259	0.62	0.80	0.90
DMF	3.86	37	139	0	0.69	0.88
DMSO	3.90	47	169	0	0.76	1.00
Methanol	1.70	34	205	0.93	0.62	0.60
Acetonitrile	3.92	38	138	0.19	0.37	0.75

differing, values of μ , ϵ , δ_H^2 , and π^* as demanded by the requirement of immiscibility with apolar liquids. Their hydrogen bonding acidity and basicity vary over a wide range. Solvents like DMF and DMSO which have no hydrogen atom available for bonding have $\alpha = 0$. The differences in the values of the parameters should help us to rationalize why some solvents can form stable emulsions similarly to water while others cannot.

In general, the emulsions showed two types of instability. The first was creaming, caused by (upward) sedimentation of oil droplets. The other was breaking, caused by coalescence of droplets, which ultimately leads to complete separation of the two phases. The part of the sample volume which contains emulsified oil therefore has two boundaries. The upper boundary is due to oil loss at the top and the lower one is the sedimentation boundary. As an example, we show in Fig. 1 the location of these boundaries as a fraction of the sample height over the course of time for an emulsion of decane droplets in formamide with a 1:1 (by weight) mixture of A-5 and A-10 as emulsifier. Thus, it represents a history of the emulsion's stability.

Initially, there was only a lower boundary due to creaming of oil droplets. This process always started immediately after preparation of the emulsions and was caused by the density difference between the two phases. This would normally give rise to a diffuse boundary as larger droplets rise faster than smaller ones. However, the process is strongly enhanced by the clustering of droplets, which is caused by the depletion mechanism (6). At emulsifier concentrations above the critical micelle concentration (cmc) there exist micelles in the continuous phase of the emulsion. These give rise to a depletion attraction between the oil droplets which causes them to cluster. The clusters are much more buoyant than the individual droplets and cream much faster. This produces a sharp fast-rising boundary. The clustering of droplets does not cause them to coalesce, however, and the droplets remain emulsified. Thus, we do not consider creaming an instability in this work.

In the case of the sample in Fig. 1 the second boundary, indicating oil loss, appears only after most of the creaming has taken place. At this point the oil concentration inside

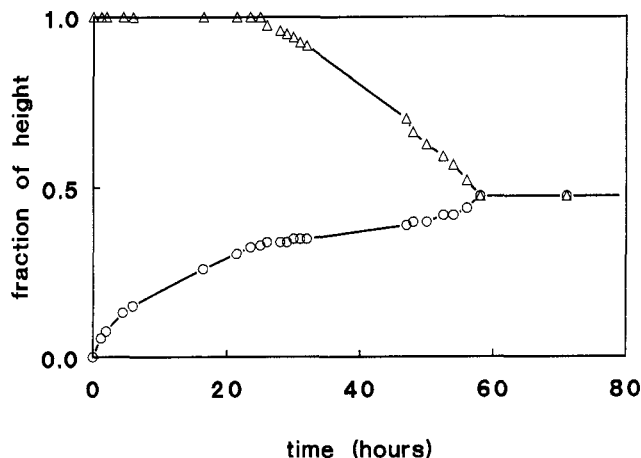


FIG. 1. History of a decane-in-formamide emulsion stabilized with a 1:1 mixture of A-5 and A-10. Triangles indicate the boundary of oil separation, circles the creaming boundary.

the emulsion is about 75%. Of course significant droplet coalescence may have occurred long before that point. This breaking instability is more serious in the sense that the emulsifier solution is no longer capable of keeping the oil emulsified. The point at which 5% of the oil has separated therefore serves as a suitable measure for the stability of the emulsion and is noted as the "time until breaking."

It has long been recognized that in a homologous series of surfactants there is a point or range in which the balance between the lipophilic and hydrophilic parts of the molecule is optimal for a specific emulsion. This is reflected in the HLB number of the surfactant, which tells how much out of balance the two parts are. In each nonaqueous surfactant system the concept of hydrophilicity should be replaced by solvophilicity, thus defining a new scale which incorporates interactions specific to that solvent. However, since this is not easily quantified and since, for polar solvents, "more hydrophilic" will in most cases imply "more solvophilic," the HLB scale can still provide a useful yardstick.

For each polar solvent, therefore, a series of surfactants was investigated ranging from very lipophilic to very hydrophilic (HLB scan). Intermediate HLB numbers were obtained by mixing two surfactants in a certain weight ratio. The mixture was assigned an HLB number equal to the weight average of the HLB numbers of the pure surfactants (7). Decane was used as the oil phase, which made up 50% v/v of the emulsion. After the sample is shaken, very viscous emulsions are obtained for water, FA, NMF, and DMSO. In Table 2 we show the time until breaking for these solvents. DMF, methanol, and acetonitrile did not show any tendency to form emulsions at all. It is clear that by far the most stable nonaqueous emulsions can be obtained with FA. However, they are not nearly as stable as aqueous emulsions. Emulsions with DMSO and NMF are even more fleeting.

A clear HLB dependency is observed for FA, but not for

DMSO or NMF. Also, as for aqueous emulsions, formamide emulsions are of the direct (O/W) type above $HLB \approx 8$, and of the inverse type (W/O) below that. The rule of thumb that the continuous phase is the one in which the surfactant is most soluble (7) thus appears to be valid for FA as well, and is not inconsistent with DMSO and NMF. In Fig. 2 the time until breaking is plotted vs HLB for the formamide emulsions (circles). The overall trend seems to suggest that the optimum HLB number for oil-in-formamide emulsions is around 18 to 20. This is not in agreement with Ref. (3), where an optimum HLB of 12 was found. However, considering that the size of the surfactant molecules increases drastically with HLB in our series, another interpretation of the data suggests that the size of the surfactant molecules contributes to the stability. This is probably due to steric stabilization. Figure 2 also clearly shows that surfactant mixtures (open symbols) form more stable emulsions than pure surfactants (filled symbols). An extra point for Brij 35 ($HLB = 16.9$) was included in Fig. 2 to show that it falls within the trend for pure surfactants but below a mixture with a similar HLB number. We also found that surfactants with HLB numbers around 8 have a strong tendency to form microemulsions in formamide systems. Nonaqueous microemulsions have been investigated recently in a variety of nonaqueous solvents among which FA (8, 9).

The suggestion that large surfactant molecules are better stabilizers for formamide emulsions than low molecular weight surfactants led us to investigate the class of PEO-PPO-PEO triblock copolymer surfactants, which has received considerable attention in recent years (4). The observed stability of emulsions with these surfactants is shown in Table 3. Indeed, emulsions with FA and DMSO remain stable much longer, even though the polymer molecules are still of a relatively low molecular weight ($<10^4$). Some FA emulsions did not show any breaking even after a month. Furthermore, emulsions that did break did so only very slowly and retained a great deal of the oil for a long time. No improvement was found for NMF, DMF, methanol, and acetonitrile again did not form emulsions. All emulsions formed were of the O/W type. Even the most lipophilic PEO-PPO-PEO surfactant (with $HLB = 2$) did not form a W/O emulsion. This may be due to the U-shape of this surfactant causing the interface to curve preferentially toward the oil phase. This time FA emulsions seem to have their optimum stability at an intermediate HLB number. Again, surfactant mixtures offer a stronger stabilizing capacity. However, for DMSO and NMF no trend is observable, just as with nonpolymeric surfactants.

Although formamide emulsions containing surfactant E20P70E20 appeared to be stable practically indefinitely, microscopic observations indicated that the average droplet size increased in time. We therefore analyzed the droplet size distribution at several times after preparation. The results are shown in Fig. 3. The initial state consisted of droplets formed

TABLE 2
Time until Breaking in Hours for Nonaqueous Emulsions

Surfactant	Without silicone oil				With silicone oil	
	Water	FA	NMF	DMSO	FA	DMSO
Brij 52	>500 ^a	>500 ^a	0	0	>500 ^a	0
Brij 52/Igepal CO-520 = 2:1		5 ^{a,b}			2 ^{a,b}	
Brij 52/Igepal CO-520 = 1:2		0 ^b			0.07 ^b	
Igepal CO-520	0 ^b	15 ^b	0	0	50	0
Igepal CO-520/Triton X-100 = 1:1		25		0	80	
Triton X-100	>500	15	0	0	18	0
Triton X-100/Igepal CO-890 = 2:1		34		0.5	32	0.75
Triton X-100/Igepal CO-890 = 1:2		53	0.058	0.7	50	0.90
Igepal CO-890	>500	41	0.050	0.5	37	0.60
Igepal CO-890/Igepal CO-990 = 1:1		51	0.033	0.6	35	1.25
Igepal CO-990	>500	41	0.025	0.8	>500	1.0

Note. A time of zero means that no emulsion is formed. Emulsions contained 10.6 wt% of surfactant and 42.2 wt% of decane. Emulsions labeled "with silicone oil" contained 1wt% of silicone oil relative to decane.

^a w/o type emulsion.

^b Forms a microemulsion.

by pushing a (coarse) emulsion through the 0.45 μm pores of a filter membrane. It is clear that the average droplet size and the width of the distribution both increase in time. Since the emulsion did not break even after a long time it seems unlikely that there is much droplet coalescence. In fact, we found that Ostwald ripening was responsible for the droplet growth. This process has been shown to be important in aqueous emulsions of lower alkanes (10–12). Since the oil in small droplets is at a higher Laplace pressure it has a higher chemical potential and it is therefore slightly more soluble in the polar phase than the oil in the larger droplets. As a result, even at low solubilities oil diffuses from the small droplets to the large droplets at a noticeable rate. Theo-

retical analysis has shown that Ostwald ripening is a second order process and causes the cubed mean droplet radius to grow linearly in time, with the rate of increase being proportional to the oil solubility in the polar phase and to its diffusivity (13). The linear relation has been confirmed experimentally (12, 14).

In Fig. 4 we verified this for the data in Fig. 3 (triangles). A linear relationship was indeed found. This does not yet prove that droplet growth is really Ostwald ripening because in an aggregation/coalescence process the aggregation step is also second order (and coalescence is first order). For the E3P43E3 emulsion, which began to break already after 23 h, however, the relation was nonlinear and was more reminiscent of a first order coalescence process. For E76P29E76, stable for 65 h, the relation was again linear, but the growth rate was much larger.

The strongest indication that droplet growth in FA emulsions involves Ostwald ripening was that it can be arrested by adding a trace amount of a completely insoluble compound to the oil phase (10, 15). In this case we added 1% w/w of silicone oil to the decane. Figure 5 shows that the droplet size distribution no longer grows with time. This is caused by the fact that, as the small droplets begin to "evaporate," they are enriched in silicone oil, which cannot leave the droplet. Large droplets grow, so that their silicone oil is diluted. This sets up a chemical potential difference opposite to the Laplace effect and brings the ripening process to a halt. Indeed, we were able to prevent ripening of emulsions of the lower alkanes isooctane and hexane in the same way.

Since Ostwald ripening proved to be so important in these nonaqueous emulsions, we reexamined the time until breaking of emulsions with 1 wt% of silicone oil added to the oil

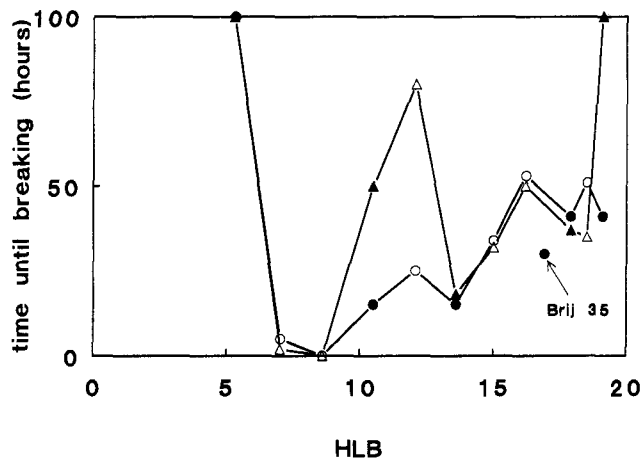


FIG. 2. Time until breaking versus HLB for emulsions in formamide. Circles: oil phase is decane. Triangles: oil phase is decane + 1% silicone oil. Closed symbols indicate pure surfactants, open symbols are mixtures. The points shown at 100 hours should be at infinity.

TABLE 3
Time until Breaking in Hours for Nonaqueous Emulsions Using the Triblock Copolymers of *EaPbEa*

Surfactant	Without silicone oil				With silicone oil	
	Water	FA	NMF	DMSO	FA	DMSO
E3P43E3	0 ^a	23	0.017	2	70	6
E3P43E3/E20P70E20 = 3:1		150		7	>1000	40
E3P43E3/E20P70E20 = 1:1		150	0.025	22	>1000	>1000
E3P43E3/E20P70E20 = 1:3		>1000		24	>1000	>1000
E20P70E20	>1000	200	0.033	23	>1000	>1000
E20P70E20/E76P29E76 = 3:1		>1000		30	>1000	>1000
E20P70E20/E76P29E76 = 1:1		>1000	0.033	21	>1000	>1000
E20P70E20/E76P29E76 = 1:3		150		20	>1000	>1000
E76P29E76	>1000	65	0	22	77	40

Note. Emulsion compositions are the same as in Table 2.

^a Surfactant insoluble in both phases.

phase. In Table 2 (right two columns) we show some of these new results for the nonpolymeric surfactants. For NMF, DMF, methanol, and acetonitrile there was no improvement, and for DMSO it was rather small. Therefore, Ostwald ripening is not the rate-determining process in emulsion breakup for these liquids. Some of the FA emulsions, on the other hand, show clear improvement in stability. These data are plotted in Fig. 2 (triangles) to compare them with the situation without silicone oil. It is clear that Ostwald ripening affects emulsion stability at HLB numbers between 10 and 13. A stability maximum now appears at around HLB = 12, in agreement with Ref. (3). The overall trend of increasing stability with surfactant size remains. Emulsions with Igepal CO-990 (HLB = 19.1) do not show any breaking at all anymore. This is probably an effect again of the large molecular size which stabilizes droplets against coalescence. Indeed, examining the new results for the polymeric surfactants in Table 3 (right two columns) it is seen that these

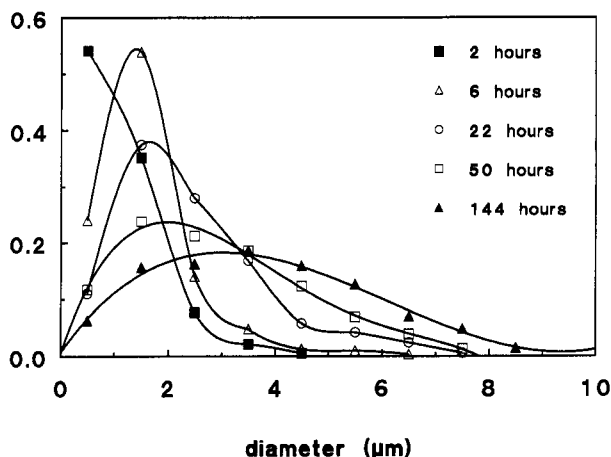


FIG. 3. Effect of Ostwald ripening on droplet size distributions of decane-in-FA emulsions at several times after preparation.

emulsions are very stable. Most specifically, DMSO emulsions stabilized with PEO-PPO-PEO also become stable indefinitely when the oil contains a trace of silicone oil. No change was observed with NMF, DMF, methanol and acetonitrile.

In Fig. 6 we show the time until breaking for an emulsion in FA stabilized with increasing E20P70E20 concentrations, both with and without the 1% silicone oil. When Ostwald ripening is prevented E20P70E20 is a very good surfactant even at low concentrations. No breaking occurs anymore above ~0.5 wt%. When no silicone oil is added the increase in stability with concentration is much more gradual. Higher surfactant concentrations therefore seem to slow down the destabilizing action of Ostwald ripening, but do not stop it.

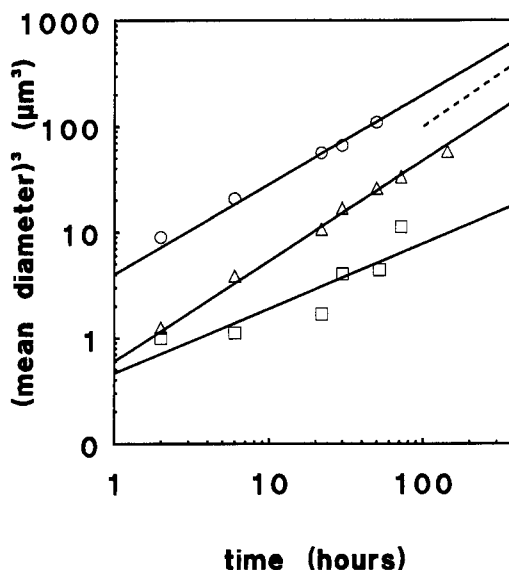


FIG. 4. The mean droplet diameter cubed versus time for decane-in-FA emulsions with surfactants (○) E76P29E76, (△) E20P70E20, and (□) E3P43E3. The dashed line indicates a slope of unity.

Thus, Ostwald ripening has a strong influence on the stability of nonaqueous emulsions. The rate of ripening for the FA emulsion with E20P70E20, which is otherwise completely stable against coalescence, is $0.5 \mu\text{m}^3/\text{h}$ (Fig. 4). This is much higher than the value $8.3 \times 10^{-4} \mu\text{m}^3/\text{h}$, reported for a 10 vol% decane-in-water emulsion stabilized with 0.1 M SDS (14), even when the difference in oil volume fraction is taken into account. (This increases the rate by roughly a factor of 2 when going from 10% to 50% of oil (16).) The faster ripening rate is probably due to a higher solubility of the oil in the nonaqueous liquid than in water. Solubility data for decane in FA are not available. The solubility of decane in DMSO is 0.7 g/100g (17) versus 1.5×10^{-6} g/100g for water (18), which explains the very short stability time of DMSO emulsions without the silicone oil. It seems likely, therefore, that the nonaqueous emulsions in earlier reports (1, 3), which were stable for at most 24 h, could also be made significantly more stable by the addition of a trace component to the droplet phase that is very insoluble in the continuous phase.

Finally, there remains the question why one polar liquid can form stable emulsions with conventional surfactants and the other cannot. It seems likely that the liquid has to resemble water in its structural properties and/or in its ability to solvate the surfactant. Formamide comes closest to this requirement (Table 1) and indeed forms the most stable nonaqueous emulsions. It is both a strong donor and acceptor of hydrogen bonds. When moving to N-methylformamide, the hydrogen bond donating ability decreases and also the number of possible H-bonds per molecule is one instead of two. The H-bond accepting ability and permittivity are higher, however. Since NMF does not form stable emulsions for longer than a few minutes the requirement of strong H-bond donating ability seems to be the decisive factor. This is confirmed by the complete inability of DMF and acetonitrile to form emulsions. This can be understood since the

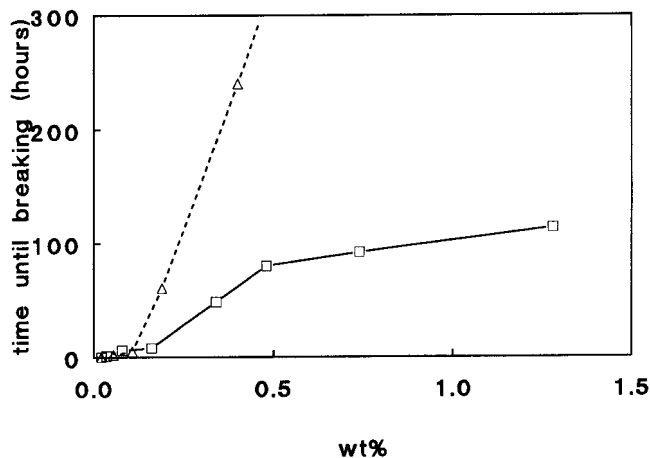


FIG. 6. Time until breaking of decane-in-FA emulsions vs surfactant weight concentration (relative to FA + surfactant). Squares: pure decane; triangles: decane + 1% silicone oil.

nonionic surfactants used contain a chain of $-\text{CH}_2\text{CH}_2\text{O}-$ units which can accept these H-bonds. However, the conclusion is completely at odds with the observation that DMSO, being only an H-bond acceptor, can form very stable emulsions. Therefore, a discussion in terms of polarity and solvating parameters alone is insufficient to explain or predict the emulsifying power of a polar liquid.

CONCLUSIONS

Stable concentrated oil-in-formamide and oil-in-dimethylsulfoxide emulsions could be prepared using commercially available nonionic surfactants. Several other polar liquids turned out not to produce stable nonaqueous emulsions with these surfactants. It is unclear exactly which combination of molecular properties determines the emulsifying capacity, but hydrogen bonding clearly plays a more important role than polarity.

The most effective surfactants were the triblock copolymers PEO-PPO-PEO. Owing to their relatively large size they could stabilize FA and DMSO emulsions against breaking practically indefinitely. FA emulsions could also be stabilized reasonably well (2 or 3 days) with polyoxyethylene alkylphenols with an optimum HLB number of around 12.

Ostwald ripening was shown to be a very important factor in the stability of these nonaqueous emulsions. The process is considerably faster than in aqueous systems because of the higher (though still low) solubility of oils in nonaqueous polar solvents. Ostwald ripening could be completely arrested by dissolving in the oil a small amount (1 wt%) of a compound with an extremely low solubility in the continuous phase. This is necessary in order to obtain completely stable emulsions.

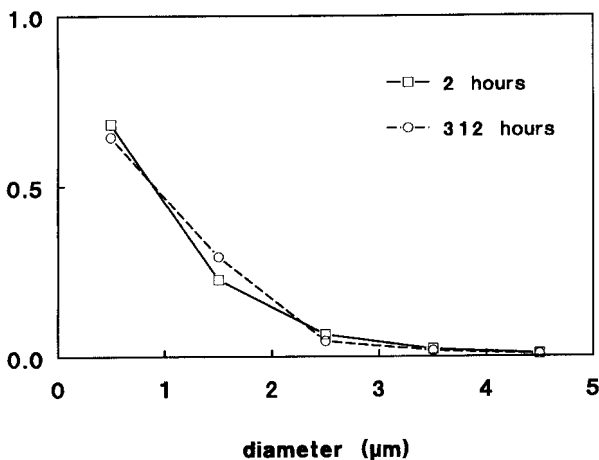


FIG. 5. Droplet size distributions of decane + 1% silicone oil emulsions in FA at different aging times.

REFERENCES

- Periard, J., Banderet, A., and Riess, G., *Polym. Lett.* **8**, 109 (1970); Riess, G., *Makromol. Chem. Suppl.* **13**, 157 (1985).

2. Nixon, J., and Beerbower, A., *Am. Chem. Soc. Div. Petr. Chem. Prepr.* **14**, 49 (1969).
3. Cameron, N. R., and Sherrington, D. C., *J. Chem. Soc. Faraday Trans.* **92**(9), 1543 (1996).
4. Nace, V. M., Ed., "Nonionic Surfactants: Polyoxyethylene Block Copolymers," Surfactant Science Series, Vol. 60. Dekker, New York, 1996.
5. Kamlet, J. M., Abboud, J.-L. M., Abraham, M. H., and Taft, R. W., *J. Org. Chem.* **48**, 2877 (1983); Abraham, M. H., Grellier, P. M., Abboud, J.-L. M., Doherty, R. M., and Taft, R. W., *Can. J. Chem.* **66**, 2673 (1988).
6. Bibette, J., Roux, D., and Nallet, F., *Phys. Rev. Lett.* **65**(19), 2470 (1990); Bibette, J., *J. Colloid Interface Sci.* **147**, 474 (1991).
7. Becher, P., "Emulsions: Theory and Practice," 2nd ed. Reinhold, New York, 1965.
8. Ray, S., and Moulik, S. P., *Langmuir* **10**, 2511 (1994).
9. Martino, A., and Kaler, E. W., *Langmuir* **11**, 779 (1995).
10. Higuchi, W. I., and Misra, J., *J. Pharm. Sci.* **51**, 459 (1962).
11. Davis, S. S., and Smith, A., in "Theory and Practice of Emulsion Technology" (A. L. Smith, Ed.). Academic Press, London, 1976.
12. Buscall, R., Davis, S. S., and Potts, D. C., *Colloid and Polym. Sci.* **257**, 636 (1979).
13. Lifshitz, I. M., and Slesov, V. V., *J. Phys. Chem. Solids* **19**, 35 (1961).
14. Kabalnov, A. S., Makarov, K. N., Pertzov, A. V., and Shchukin, E. D., *J. Colloid Interface Sci.* **138**, 98 (1990).
15. Davis, S. S., Round, H. P., and Purewal, T. S., *J. Colloid Interface Sci.* **80**, 508 (1981).
16. Voorhees, P. W., *J. Stat. Phys.* **38**, 231 (1985).
17. Jacob, S. W., Rosenbaum, E. E., and Wood, D. C., "Dimethyl Sulfoxide," Chap. 2. Dekker, New York, 1971.
18. Shaw, D. G., Ed., "Hydrocarbons in Water and Seawater. Part II. Hydrocarbons C8 to C36," Solubility Data Series, Vol. 38. Pergamon, Oxford, 1989.