$$\rho_{M,t} = M[59.21 \times 10^{-4} - 8.81 \times 10^{-6} (t) + 105.39 \times 10^{-5} (230.2 - t)^{0.3045}] \quad (11)$$

Table V is a tabulation of the densities and molar volumes of uranium hexafluoride of selected molecular weights at various temperatures. The molecular weights selected correspond closely to pure $U^{238}F_6$, $U^{236}F_6$, $U^{235}F_6$, and $U^{234}F_6$. The liquid densities are calculated from Equations 10 and 11 and the molar volumes from Equations 6 and 7, below and above 90° C., respectively.

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Effects of Surfactants on Coalescence Rest Times of Drops

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Data are reported for the rest times of drops coalescing at a flat interface in the presence of a chemically pure surface active agent. Benzene-water and water-benzene systems were used with seven surface active agents. Rest time distributions were essentially Gaussian. Film drainage time followed by a rupture time showed an exponential decay pattern. Values reported included average, minimum, maximum, median, and drainage times and the rate of rupture constant.

IF TWO nearly immiscible liquids be intimately mixed by a turbulence-creating device in the absence of a surface active agent, a temporary emulsion will form. If allowed to settle in a quiescent environment, the primary break will occur in seconds or a few minutes. A secondary emulsion, consisting of micron and submicron size droplets of the dispersed phase, will usually persist in one of the bulk phases. To separate the dispersed phase from such a dispersion it is necessary to coalesce the submicroscopic droplet into large ones of settleable size. One measure of the difficulty of the coalescence operation is the rest time of large drops at a flat interface between large volumes of the two phases. Recent reviews by Hartland (*5*) and Lawson (*8*) treat the theoretical and experimental aspects of the determination of rest time and its significance. In the present instance we are concerned not only with rest time criteria but with the effect of definable surface active agents upon them.

EXPERIMENTAL

The equipment used for the determination of drop rest time was slightly modified from that of Charles and Mason (*1*) and was similar to that used by others (*2, 3, 4*). An open-top cell design was used to facilitate construction, cleaning, and assembly. One of the two coalescent cells (*6*) was designed for using an organic continuous phase. The aqueous drops were allowed to fall to the interface. The other cell was so constructed that a light drop of an organic liquid could be released from a submerged nozzle and rise through a continuous aqueous phase to the interface. Provision was made for renewal of the interface by periodic flushing with the aqueous phase. The temperature of the water bath surrounding the cell was controlled to ±0.5° C. An electric timer was used to determine rest time. Its 0.01-second scale divisions were so spaced as to permit estimations of 0.001 second, although the accuracy of such an estimation was somewhat questionable. Drop volumes were measured with a microburet.

The two cells are illustrated in Figure 1. The open top, *A*, was covered with clean hard paper during operation to prevent contamination. The continuous phase was contained in the central portion across the top of the inner cup, *B*, which was used for the renewal of the organic-aqueous interface. The side arm, *C*, permitted waste liquid to be removed from the cell. The drop was released from

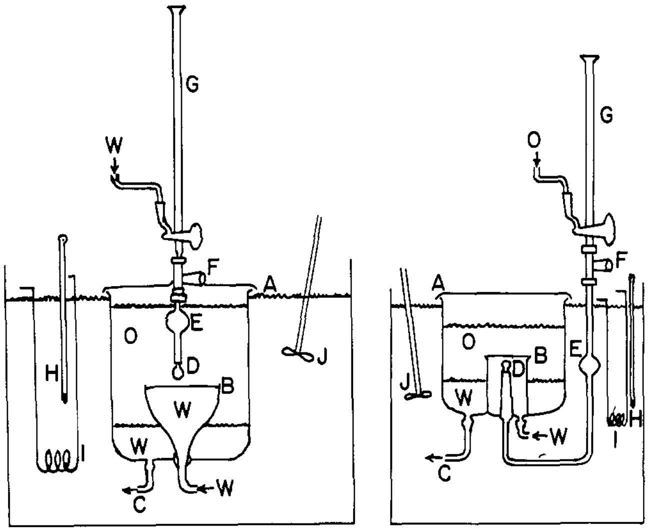

Figure 1. Diagram of coalescence cells

Left. Falling drop *Right.* Rising drop

A. Coalescence cell mouth
B. Continuous phase removal
C. Waste liquid suction
D. Drop forming tip
E. Reservoir
F. Micrometer
G. Microburet
H. Thermometer
I. Heater
J. Stirrer

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the interchangeable nozzle, *D*, connected to a reservoir, *E*, which provided sufficient residence time to ensure temperature equilibrium. Fresh drop liquid was introduced from the microburet, *G*, through the micrometer, *F*, which permitted the drop formation to proceed at a desired rate. All connecting tubes were of polyethylene. Valves were of Teflon or stainless steel.

Interfacial and surface tension measurements were carried out with a Cenco-Du Nuoy Tensiometer.

The distance from the tip of the drop to the interface was kept within 5mm. to avoid impact effects. The micrometer, *F*, was adjusted to a desirable opening to allow the drop to remain on the nozzle for 1.5 to 2 minutes in order to come to thermal and mass equilibrium. Rest time, *t*, was read on the electric timer, the smallest digit being an estimated value. Drop volume was read directly on the microburet to ±0.01 ml. After each group of eight drops, the interface was renewed and made planar. The heavier phase was periodically drawn out through side arm C.

The drop and field fluids (benzene, monochlorobenzene, styrene, and benzyl alcohol) were of the highest purity available from laboratory supply companies. Surfactants used in industrial operations are usually a mixture of rather uncertain purity. Some are soluble in both organic and aqueous phases. Some, while soluble in organic solvents, will hydrolyze when such solutions are intimately in contact with water. To avoid these uncertainties, the surfactants chosen were definite chemical compounds of the highest purity (as certified by the Fisher Scientific Co.). The sole exception was TMN (trimethyl nonyl ether of hexaethylene glycol) Tergital, supplied by the Union Carbide Chemicals Co. It is insoluble in benzene if first dissolved in water. A series of surface tension tests was carried out to be certain that the two phases were mutually saturated before the beginning of each run. The properties of the various solutions are given in Table I. The abbreviations of the proper names of all liquids used are given at the bottom of Table II.

Table I. Experimental Results of Interfacial Tensions and Surface Tensions

Oil-Soluble Surfactant			
Surfactant (in continuous phase)	Interfacial tension, dynes/cm.	Surface tension dynes/cm.	
		Benzene	Water
None	34.2	28.8	71.2
Stearic acid			
0.01*M*	28.4	28.45	71.0
0.05*M*	25.7	28.2	69.9
0.1*M*	20.0	28.2	69.7
Oleic acid			
0.005*M*	24.9	28.35	63.4
0.01*M*	23.1	28.35	62.0
0.05*M*	20.35	28.2	58.5
Cholesterol			
0.001*M*	27.2	28.2	68.5
0.002*M*	22.6	28.0	66.6
0.005*M*	17.8	28.0	64.4

Water-Soluble Surfactant			
Surfactant (in continuous phase)	Interfacial tension, dynes/cm.	Surface tension dynes/cm.	
		Benzene	Water
None	34.2	28.8	71.2
Ethyl hexadecyl dimethylammonium bromide			
0.0005*M*	2.4	28.2	37.12
0.001*M*	1.2	28.15	37.08
0.01*M*	2.1	28.3	33.6
TMN			
0.01*M*	15.5	28.6	41.4
Sodium lauryl sulfate			
0.005*M*	4.2	28.5	34.0
Sodium decyl benzenesulfonate			
0.008*M*	3.0	28.4	31.2

Table II. Rest Time Data

Run No.	Drop Phase	Containing Phase	Surfactant	Drop Vol., Ml.	Rest Times, Sec.				Drain Time, t_o	Rate of Rupture Constant, *K*, Sec.$^{-1}$
					$\bar{t}$	$t_{\min}$	$t_{\max}$	$t_{1/2}$		
101	BA	W	...	0.128	2.538	1.050	5.966	...	...	...
103	W	S	...	0.296	1.499	0.460	2.762	...	...	...
105	CB	W	...	0.318	11.682	1.620	25.351	...	...	...
106	W	B	...	0.298	3.190	0.682	5.348	...	...	...
201	W	B	...	0.307	4.852	0.890	10.971	...	...	...
203	W	B	...	0.301	4.938	1.387	13.029	4.3	2.8	0.456
204	W	B	...	0.302	4.986	0.874	11.200	4.55	2.98	0.443
205	W	B	...	0.308	5.774	1.430	16.010	...	...	...
208	W	B	...	0.300	4.595	0.960	10.210	...	...	...
301	W	B	StA (0.01*M*)	0.302	7.213	3.297	13.745	6.4	4.5	0.370
303	W	B	StA (0.05*M*)	0.301	8.733	4.150	14.522	8.2	6.2	0.346
305	W	B	StA (0.1*M*)	0.300	9.626	5.274	14.872	9.05	6.95	0.329
311	W	B	OA (0.005*M*)	0.302	7.400	2.981	17.746	6.95	5.00	0.356
313	W	B	OA (0.01*M*)	0.300	8.012	4.230	15.883	7.15	5.12	0.341
314	W	B	OA (0.05*M*)	0.300	9.652	3.607	19.232	8.15	5.2	0.238
321	W	B	Ch (0.005*M*)	0.195	27.930	10.285	58.220	24	13	0.685
322	W	B	Ch (0.001*M*)	0.200	10.144	6.321	15.213	...	...	...
323	W	B	Ch (0.002*M*)	0.2	17.809	6.244	36.683	16	12	0.1658
401	B	W	EDAB (0.001*M*)	0.017	206.633	70.421	397.385	178	117	0.0114
402	B	W	EDAB (0.005*M*)	0.015	115.880	48.280	254.350	105	71	0.0202
403	B	W	EDAB (0.0005*M*)	0.015	155.249	57.686	312.245	146	108	0.0184
411	B	W	TMN (0.01*M*)	0.205	14.674	6.820	20.470	12.9	10.7	0.311
412	W	B	TMN (0.01*M*)	0.105	3.378	1.110	6.510	2.15	1.14	0.782
421	B	W	SLS (0.005*M*)	0.038	94.620	38.365	185.376	92	71	0.0338
422	B	W	SDBS (0.008*M*)	0.055	126.061	52.734	231.250	128	98	0.0228

BA, benzyl alcohol. W, water. S, styrene. CB, monochlorobenzene. StA, stearic acid. OA, oleic acid. Ch, Cholesterol. EDAB, ethyl hexadecyl dimethyl ammonium bromide. TMN, Trimethyl nonyl ether of hexaethylene glycol (Union Carbide Chemicals Co.). SLS, sodium lauryl sulfate. SDBS, sodium decyl benzene sulfonate.

Since the surface active chemicals used were of the highest purity available, it was assumed that the effects of the slight amounts of impurities present could be neglected. It was qualitatively estimated that such impurities, if present, acted as some low molecular weight compounds acting through the Marangoni effect. Their effect on the rest time would therefore be unobservable.

It was assumed that all drops were spherical and that the interfaces were flat. For the systems used in this work and in the apparatus employed, these were good approximations. External mechanical influences were minimized and assumed to have negligible effect on the results. Only major film-thinning forces were considered, and minor phenomena such as electroviscosity, electric double-layer repulsion, internal circulation, etc., were assumed to be negligible for the rest time evaluation.

CORRELATION OF DATA

The theoretical background and its logical application may be found in previously published papers (*1–8*). The main points are:

The relationship between the fraction of drops coalesced, *f*, when plotted against the rest time, *t*, should exhibit an approximately Gaussian distribution. When plotted on probability paper, the points should lie along a straight line. This test of the nature of the distribution of rest times is seldom reported.

The equation,

$$\ln N = \ln (1 - f) = - K (t - t_0)^x \qquad (1)$$

will generally represent the rest time distribution. Gillespie and Rideal (*4*) found x to be 1.5, while Cockbain and McRoberts (*2*) found it to be unity. Elton and Picknett (*3*) recommend $x = 1$. The present work indicates $x = 1$.

The value of t_0 can be obtained by reading it from the intercept on the *t*-axis of the straight-line portion of a plot of Equation 1 or calculated as

$$t_0 = t_{1/2} - (1/K) \ln 2 \qquad (2)$$

The value of $t_{1/2}$ may be read from the plot or by noting its value at the midpoint of a series of observations arranged in order of magnitude. In the latter method, it may not be on the best straight line drawn through the points.

The effect of a surfactant is to increase the rest time. The usual expression for this relationship is (*2*)

$$t_{1/2} = k_c C^m \qquad (3)$$

but the present work indicates that a better correlation is obtained by using the arithmetic mean rest time, $\bar{t}$, instead of the median value, $t_{1/2}$.

The important criteria in the present investigation are summarized in Table II. The 40 individual measurements from which the plots were made may be found in the thesis by Hsu (*6*). Values for run 204, illustrated by Figure 2, are given in Table III.

Constants in Equation 3 are given in Table IV for those surfactants for which runs at different concentrations were made. The average rest time, $\bar{t}$, was used in this correlation.

DISCUSSION OF RESULTS

For the benzene-water system the stabilities of the individual drops varied. The results followed a Gaussian distribution curve sufficiently reproducible for analysis. Initially, 50 drops were taken for a run, but it was found later that 40 coalescence measurements were enough. If the fraction of uncoalesced drops, N, was plotted against time, an exponential decay distribution was obtained as in Figure 2. Such a distribution curve indicates that the lifetimes of the drops are determined by two distinct processes—drainage of the continuous phase between the drop and the interface, followed by rupture of the adsorbed film.

Analysis of data also showed that most of the results of this investigation gave straight lines for the fraction of uncoalesced drops, N, between 0.05 and 0.60.

This work proposes that the action of a surface active agent is not only to increase the viscosity of the continuous phase, thereby decreasing the rate at which two interfaces can approach each other, but also to reduce the interfacial tension, thereby decreasing the rate of film rupture. It was observed in the experiments (Table II) that surfactants change the mean rest time more effectively than the minimum rest time. This indicates that surfactants have somewhat less effect on the drainage of liquid between interfaces than upon the nature of interface itself.

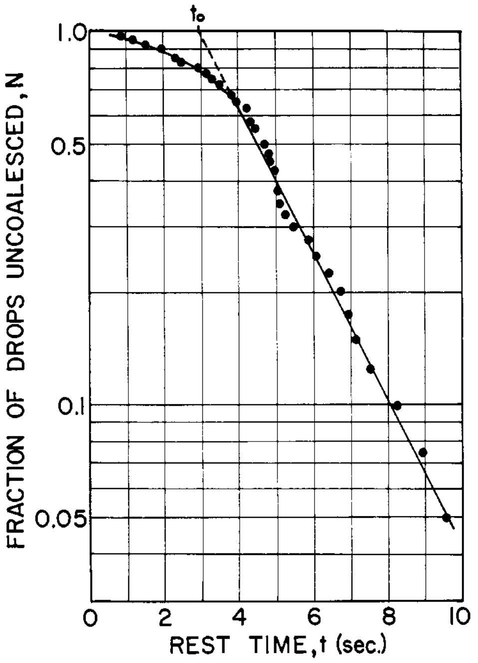

Figure 2. Semilogarithmic rest time distribution of water drops through benzene
Run 240

Table III. Rest Time of Water Drops Dispersed in Benzene

(Run 204)

Rest Time, Sec.

Group 1		Group 2		Group 3		Group 4		Group 5	
1	4.980	9	6.432	17	5.128	25	3.585	33	5.270
2	2.505	10	1.954	18	10.110	26	1.203	34	5.043
3	5.886	11	3.541	19	4.450	27	7.543	35	3.320
4	1.547	12	3.885	20	4.345	28	4.775	36	4.703
5	8.988	13	4.120	21	0.974	29	5.005	37	2.201
6	4.870	14	8.310	22	4.805	30	5.498	38	9.541
7	11.200	15	6.130	23	3.950	31	2.981	39	4.632
8	6.902	16	2.288	24	7.155	32	3.147	40	6.742

Table IV. Constants in Rest Time–Concentration Correlation[a]

Surfactant	m	k_c
Stearic acid	0.141	13.2
Oleic acid	0.134	14.64
Cholesterol	0.535	410

[a] Rest time-concentration correlation $\bar{t} = k_c C^m$.

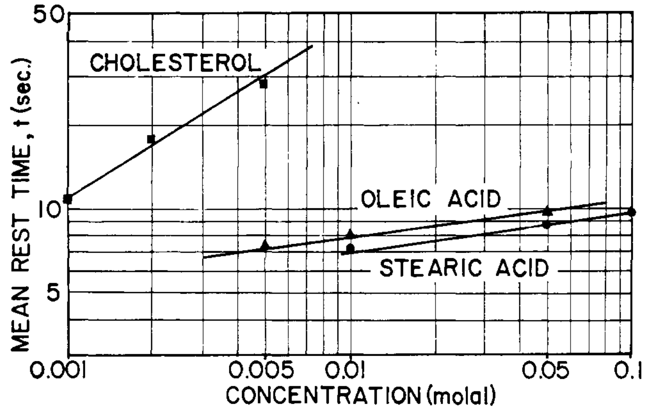

Figure 3. Mean rest time as a function of concentration of surfactant

Besides the above observations, this work led to the following:

Drainage Time, t_0. For time greater than the drainage time, t_0, a linear relationship was obtained for the logarithmic rest time distribution calculated by $t_0 = t_{1/2} - (1/K) \ln 2$. This agrees with the theory used to develop this equation, since it assumes the interfacial rupture process dominates after time t_0. Thus the use of this equation is supported by this work.

Mean Rest Time, $\bar{t}$. Table II shows that $\bar{t}$ represents the stability of the system better than $t_{1/2}$, $t_{\min}$, or $t_{\max}$. This has been also checked by the fact that $\bar{t}$ could be correlated to concentration of surfactant as shown in Figure 3. Thus, it is reasonable to take the arithmetic mean rest time $\bar{t}$ as the criterion to represent the stability of a system.

Concentration of Surfactant. As the concentration of surfactant increases, the rest time increases correspondingly; the K value (Table II) decreases as the range of rest time is broadened. Furthermore, the mean rest time, $\bar{t}$, could be correlated as shown in Figure 3 by the relation $\bar{t} = k_c C^m$ where parameters k_c and m are different for each system (Table IV).

Saturation or Unsaturation. Run 106 shows that the unsaturated benzene gave a shorter mean rest time of 3.19 seconds, while the saturated system gave approximately 4.94 seconds. The mutually saturated phases normally give longer lifetimes than the unsaturated phases. This effect is noticeable even when the solubility is very slight.

Stability of Water-Oil or Oil-Water Emulsion. It was clearly indicated by the nonionic surfactant study (TMN) that for the same oil-water interface, benzene drops coalesced with the bulk oil phase at a rate which differed from the rate of coalescence of water drops. This indicates that oil drops are stabilized by water-soluble surfactants, and water drops are stabilized by oil-soluble surfactants. The results of this work in general agree with the concept advanced by earlier workers that some part of the drop must "wet" the bulk liquid before coalescence can occur. If the surfactant is soluble in water and insoluble in the oil, it will collect on the outside of oil drops and tend to prevent their coalescence. However, if the drops are water instead of oil, the surfactant is inside the drops and as the molecules of surfactant are free to move into the drops, there is very little film to prevent coalescence when the drop comes in contact with the interface.

Critical Micellar Concentration (CMC). The K value decreased with increasing concentration of ethyl hexadecyl dimethyl ammonium bromide (EDAB water-soluble surfactant) from $0.0005M$ to $0.001M$ and then increased as EDAB increased to $0.005M$. This means that mean rest time reaches a maximum near the concentration of $0.001M$. Cockbain and McRoberts (*2*) reported that the critical micellar concentration of EDAB was about $0.0008M$. This is consistent with the previous suggestion (*2*) that oil drops possess maximum stabilities at concentrations slightly greater than the critical micellar concentrations.

Partial Coalescence. Through all the experiments, the drops did not coalesce completely with the bulk phase in a single stage. Partial coalescence occurred, leaving a smaller drop which, in turn, partially coalesced again. Generally speaking, this phenomenon was observed in the presence of low concentrations of surfactants. But at higher concentrations where the interfacial tensions were very low, coalescence appeared to occur in a single stage.

NOMENCLATURE

C = concentration of surfactant, molar
f = fraction of drops coalesced
K = rupture constant in Equation 1, sec.$^{-1}$
k_c = coefficient in Equation 3
m = exponent in Equation 3
N = $(1 - f)$ = fraction of drops uncoalesced
t = rest time of drop at interface, sec.
t_0 = t − intercept of straight-line portion in plot ln N *vs.* t, sec.
$t_{1/2}$ = median rest time of large number of drops of specific size, sec.
$\bar{t}$ = arithmetic mean rest time of large number of drops of specific size, sec.
$t_{\min}$ = lowest value of t in series, sec.
$t_{\max}$ = largest value of t in series, sec.
x = exponent in Equation 1

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