REFERENCES

1. Lobo, P. A., D. C. Coldiron, L. N. Vernon, and A. T. Ashton, Chemical Engineering Progress, *58*, 85–88 (1962).
2. Terry, B. W., and W. L. Groves, Petroleum Refiner, April 1961, pp. 147–149.
3. Hinds, G. E., Petrochemical Industry, Feb., 1959, pp. 7–9.
4. Waddelow, R. W., and E. L. Hatlelid, presented at the American Chemical Society Southwest Regional Meeting, Oklahoma City, Dec. 1, 1960.
5. Du Pont, U. S. Patent 2,395,240, Feb. 19, 1946.
6. Deutsche Hydrierwerke, Ger. Patent 723,837, Aug. 18, 1942.
7. Reid, E. Emmet, "Organic Chemistry of Bivalent Sulfur," Vol. 1, p. 21ff (1958).
8. Smiley, R., J. Org. Chem., *25*, 257 (1960).
9. Deutsche Hydrierwerke, Ger. Patent 611,924, April 9, 1935.
10. Farben, I. G., U. S. 2,043,965, June 9, 1936.
11. Westphal, O., et al., Ber. *73B*, 1002–11 (1940); Chem. Abs., *35*, 3599 (1941).
12. Chemical Week, Dec. 30, 1961, pp. 36, 37.
13. Procter & Gamble, U. S. 2,999,068, Sept. 5, 1961.
14. Procter & Gamble, U. S. 3,001,945, Sept. 26, 1961.
15. Unilever, N. V., Belgian Patent 603,337, May 3, 1961.
16. Procter & Gamble, South African 60/5076, Nov. 30, 1960.
17. The Firestone Tire and Rubber Co., U. S. 2,755,258, July 17, 1956.
18. Monsanto Chemical Co., U. S. 2,964,131, Dec. 13, 1960.
19. Monsanto Chemical Co., U. S. 2,687,442, Aug. 24, 1954.
20. Monsanto Chemical Co., U. S. 2,628,951, Feb. 17, 1953.
21. Standard of Indiana, U. S. 3,007,784.
22. "Unichem," U. S. 2,094,489, Sept. 28, 1937.
23. Procter & Gamble, U. S. 2,989,547, June 20, 1961.
24. Standard of Indiana, U. S. 2,926,182, Feb. 23, 1960).
25. Pratt, E. F., et al., J. Am. Chem. Soc., *76*, 52–56 (1954).
26. Sulzbacher, M., J. App. Chem., *5*, 637–641, Dec. 1955.
27. Unpublished.
28. Fawcett, E. W., J. Chem. Soc., 396–400 (1934).
29. Hoh, G. L. K., et al., JAOCS, in press.

[Received September 13, 1962—Accepted October 23, 1962]

Foaming Properties of Nonionic Detergents [1]

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Abstract

The foam formation and foam stability of aqueous solutions of polyoxyethylene tridecanols, t-octylphenols, nonylphenols, n-dodecanols, and n-octadecanols have been determined as a function of ethylene oxide chain length. In general nonionic detergents form unstable foams; the most stable foams formed by nonionic detergents are comparable to that of sodium dodecylbenzene sulfonate in the absence of foam promoters. In each homologous series of a nonionic detergent the foam formation and foam stability pass through a max at a critical hydrophilic-hydrophobic balance (CHHB). It is shown that the CHHB corresponds to conditions of minimum foam drainage and max resistance to film rupture.

Introduction

IN SPITE OF the expanding application of nonionic detergents, relatively few papers on their foaming properties have appeared in the literature compared to those of ionic detergents, because monodisperse materials are difficult to prepare (1,2,3). Their synthesis has been reported so far for a chain length of one to six ethylene oxide units only (4). Nonionic detergents, which have been prepared by the condensation of ethylene oxide with alkylphenols or aliphatic alcohols, yield products in which the hydrophilic portion has a Poisson distribution of chain length (5). In order to cover a wide range of molecular structures, molecularly distilled ethylene oxide condensates of alkylphenols or aliphatic alcohols have been used in this investigation of the foaming properties of nonionic detergents in aqueous solutions (6). Since in practical applications detergent solutions are mainly used at elevated temps, this investigation was carried out at 55.0C.

The principal factors determining the stability of foams have recently been reviewed by DeVries, Kitchener and Cooper, and Mysels et al. (7,8,9). The collapse of foam involves two main factors: (1) Film drainage and (2) film rupture. The foam lamella must first drain until its thickness is reduced to 50–100Å, after which it will eventually rupture. The rate of drainage is primarily dependent on the viscosity of the absorbed film. Hence, a high surface viscosity leads to a slow-draining and stable film, or vice versa. Measurements of surface viscosity or of the rate of movement of interference fringes, which has been so successful in the study of slow-draining foams of ionic detergents, were unsuccessful when applied to fast-draining foams of nonionic detergents (9,10,11), On the other hand the foam fractionation technique of Walling et al. appeared to be applicable to this study (3). The film rupture is dependent on the cohesive forces (Gibbs' elasticity) existing in the adsorbed film, whose magnitude has been deduced from the molecular configurations of nonionic detergents in adsorbed films. A detailed study of these configurations has already been reported elsewhere (6).

Experimental Procedures and Data

Materials. The ethylene oxide (EO) condensates of branched tridecanol, t-octylphenol, branched nonylphenol, n-dodecanol, and n-octadecanol have been obtained from General Aniline and Film Corp., Monsanto Chemical Co., and Rohm and Haas Co. All samples were molecularly distilled in order to remove unreacted components and reduce the width of the mol wt distribution. The average chain length of the ethylene oxide adducts was determined from their hydroxyl values, and their homogeneity was assessed from the sharp breaks in the surface tension vs. logarithm of concentration plots, which correspond to the critical micelle concentration (c.m.c.) (6). All nonionic detergents used exhibited sharp breaks. The sodium dodecylbenzene sulfonate (NaDDBS) was of 99.9% purity. Distilled water of 2×10^{-6} mho/cm specific conductance was used.

Procedures. The foaming properties were determined with a piston plunger agitator equipped with perforated disks. The stroke length was 5 in. and the stroke speed 56 cycles/min. The detergent solutions, 200 ml, were contained in covered graduated cylinders, which were thermostated at 55.0C. The foam formation is expressed as ml of foam volume generated after 15 min agitation and the foam stability as the time required for the foam volume to decay to one half of the initial height in the closed system after agitation has been halted. The foam drainage properties of 0.1% w. detergent solutions were determined by the method of Walling et al. at 55.0C (3). This procedure gives useful results primarily with rapidly draining films in which the loss of liquid from the foam occurs mainly by loss of water from the films of the intact foam lamellae. The apparatus consists of a 5 liter spherical vessel with a heating mantle, interchangeable columns of 9.4 cm i.d. and a

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[1] Paper presented in part at the 34th National Colloid Symposium, Lehigh University, Bethlehem, Pa., 1960.

lucite collector head. The total column height varies from 15, 45.5, 76 to 137 cm. The foam was generated by bubbling air through a sintered glass disk at a const rate. The initial rate of foam rise was 0.32 cm/sec. The foam wt was determined by weighing the collector head. The draining time is defined as the time required for the foam to rise from the solution level to the top of the column. The surface chemical measurements have been described elsewhere (6).

Data. The foam formation and foam stability of aqueous solutions of polyoxyethylene tridecanols, t-octylphenols, nonylphenols, n-dodecanols, and n-octadecanols have been determined as a function of ethylene oxide chain length at 55.0C over a concentration range from 10^{-6} to 10^{-3} M/l (and for the homologs of tridecanol from 10^{-6} to 10^{-2} M/l). By way of illustration the foaming data of polyoxyethylene tridecanols are given in Figure 1, in which the corresponding c.m.c. values are indicated by arrows (6). With increasing detergent concentration the foam formation and foam stability rise and reach a plateau region at concentrations considerably above the c.m.c. This may be attributed to time effects in adsorption rate, which are significant with nonionic detergents and decrease with increasing detergent concentration (6). In each homologous series of a nonionic detergent the foam formation and foam stability pass through a max at a critical hydrophilic-hydrophobic balance (CHHB) as shown in Table I, which represents the data in the plateau region at a concentration of 10^{-3} M/l. For comparison the data of sodium dodecylbenzene sulfonate are included in Table I. In general, nonionic detergents form unstable foams; the most stable foams formed by nonionic detergents are comparable to that of sodium dodecylbenzene sulfonate in the absence of foam promoters. In order to explain the max in foam formation and foam stability at the CHHB, the two factors determining the collapse of foam, (1) film drainage and (2) film rupture have been examined separately and the pertinent data are given in the following tables.

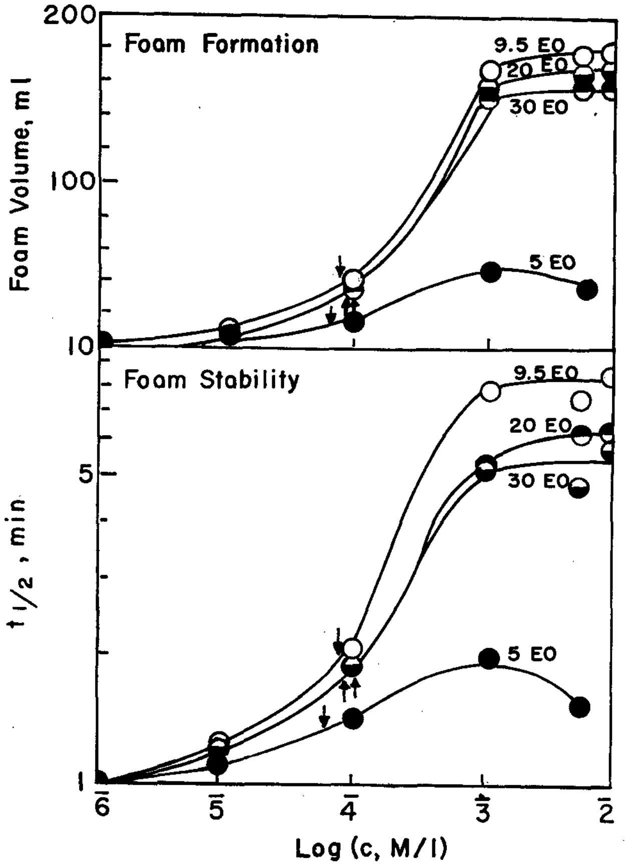

FIG. 1. Foaming properties of tridecanol + n EO solutions at 55.0C (arrows signify the c.m.c.).

A comparison of the foam drainage properties of sodium dodecylbenzene sulfonate with several nonionic detergents is given in Table II. The initial rate of foam rise was maintained constant, but the column heights were varied. For the hypothetical case of no loss of liquid due to drainage, no variation of foam wt with increasing draining time would be expected. It follows from the appreciable decrease in foam wt with increasing draining time that these nonionic detergents form fast draining foams comparable to that of sodium dodecylbenzene sulfonate. This is in line with their low foam stability. The rate of drainage is proportional to the wt of foam collected as may be deduced from the plot of the logarithm of foam wt vs. draining time, which is linear up to draining times of 500 sec. Loss of liquid from the foam lamellae due to bubble rupture is insignificant. In addition the drainage properties of each homologous series of nonionic detergents are given in Table III for a single column height. In general agreement between foam drainage from Table III and foam stability from Table I was observed. In each homologous series a minimum in foam drainage, i.e. a max in foam wt collected, was observed at the CHHB.

TABLE I

Foaming Properties of Nonionic Detergents at c=10^{-3} M/l and 55.0C

Hydrophobic group	No. of C atoms in straight chain hydrophobic group	n-EO	Foam formation, foam volume, ml	Foam stability, t½, min.	Estimated hydrophilic-hydrophobic balance[a]
NaDDBS	....	....	160	10	....
Tridecanol (branched)	9	5	40	2	0.6
		9.5	170	8	1.1(CHHB)
		20	160	5	2.2
		30	150	5	3.3
t-Octylphenol (branched)	9.5	5	40	2	0.5
		10	160	6	1.1
		20	170	15	2.1(CHHB)
		30	150	12	3.2
Nonylphenol (branched)	10.5	4	10	1	0.4
		6	150	5	0.6
		10	150	5.5	1.0
		30	170	7	2.9(CHHB)
		50	165	6.5	4.8
n-Dodecanol	12	4	50	7	0.3
		7	190	11	0.6(CHHB)
		14	160	6	1.2
		23	150	5	1.9
		30	145	3	2.5
n-Octadecanol	18	5	0	0	0.3
		14	180	14	0.8(CHHB)
		100	110	4.5	5.6

[a] Estimated hydrophilic-hydrophobic balance is the ratio of the number of EO units in hydrophilic group to the number of C atoms in straight chain part of hydrophobic group, e.g. in n-dodecanol the ratio is 7/12 = 0.58. A benzene ring is assigned 3.5C atoms.

The film rupture is dependent on the cohesive forces existing in the adsorbed film. In order to deduce the magnitude of these cohesive forces, the

TABLE II

Foam Drainage Properties of Nonionic Detergents at 55.0C

Detergent, 0.1% w	Column height, cm	15	45.5	76	137
NaDDBS	Draining time, sec	55	200	300	430
	Foam wt, g/hr	1060	700	395	320
Tridecanol + 9.5 EO	D.t., sec	35	165	320	620
	F.W., g/hr	1160	734	406	340
n-Dodecanol + 14-EO	D.t., sec	65	205	340	596
	F.W., g/hr	1434	710	344	120
Nonylphenol + 10 EO	D.t., sec	40	180	290	560
	F.W., g/hr	563	492	319	280
t-Octylphenol + 10 EO	D.t., sec	50	194	284	573
	F.W., g/hr	1710	922	784	380

TABLE III

Foam Drainage Properties of Nonionic Detergents at a Single Column Height and 55.0C

Detergent, 0.1% w	Foam wt, g/hr, collected at top of 137 cm column	Estimated hydrophilic-hydrophobic balance
Na DDBS	320	....
Tridecanol + 5 EO	190	0.6
9.5	340	1.1 (CHHB)
30	300	3.3
t-Octylphenol + 5 EO	48	0.5
10	380	1.1
20	400	2.1 (CHHB)
30	350	3.2
Nonylphenol + 6 EO	70	0.6
10	280	1.0
30	310	2.9 (CHHB)
50	290	4.8
n-Dodecanol + 4 EO	58	0.3
7	280	0.6 (CHHB)
14	120	1.2
n-Octadecanol + 5 EO	16	0.3
14	380	0.8 (CHHB)
100	300	5.6

TABLE IV

Molecular Areas of Nonionic Detergents in Adsorbed Films at 55.0C

Detergent	Molecular area, Å^2 at π=20 dynes/cm
Tridecanol + 5 EO	58
9.5	71
30	87
t-Octylphenol + 10 EO	68
20	75
30	89
Nonylphenol + 10-EO	62
30	74
50	115
n-Dodecanol + 7 EO	46
14	65
23	80
30	105
n-Octadecanol + 5 EO	40
14	92
100	145

molecular configurations of nonionic detergents in adsorbed films have been determined from the molecular areas at a surface pressure of $\pi = 20$ dynes/cm, which are listed in Table IV (6). These data have been derived from surface tension vs. logarithm of concentration curves by the Gibbs' equation. The molecular areas are considerably larger than the cross-sectional areas of the aliphatic hydrocarbon chains, 20 Å^2, or of the benzene rings, 25 Å^2, and increase in each homologous series of a nonionic detergent with increasing ethylene oxide chain length. *Variations in the structure of the hydrophobic group* at constant ethylene oxide mole ratio have a small effect on the molecular areas in contrast to variations in the length of the ethylene oxide chain. From this cursory examination and the more extensive study reported elsewhere, it is concluded that the amphipathic molecules orient at the air/water interface with the hydrophobic groups in the air and the ethylene oxide chains forming coils in the aqueous phase (6). The size of the coils increases with increasing ethylene oxide chain length, and consequently the inter- or intramolecular distances between the ether oxygens increase. These distances play a vital role in determining the magnitude of the cohesive forces as will be shown in the discussion.

Discussion

The object of this investigation was to explain the max in foam formation and foam stability at the CHHB in each homologous series of a nonionic detergent. The CHHB corresponds to conditions of minimum foam drainage, which is in line with the max in foam stability at the CHHB. It also may be shown that the CHHB corresponds to conditions of max resistance to film rupture, which is another requirement for the max in foam stability. The resistance to film rupture is dependent on the magnitude of the cohesive forces existing in the adsorbed film. The cohesive forces are the summation of the van der Waals' forces between the hydrophobic groups and of inter- or intramolecular hydrogen bonding forces operating between the ether oxygens of the hydrated ethylene oxide coils.[2] Their magnitude may be deduced from the molecular configurations in the surface films. It has been shown that in each homologous series the size of the ethylene oxide coils increases with increasing number of chain segments. From this follows that the spacing between neighboring hydrophobic groups in the air/water interface increases with increasing coil size, and consequently the van der Waals' forces decrease. Thus, from consideration of the van der Waals' forces alone, a continuous decrease in cohesive forces with increasing length of the hydrophilic group is expected. On the other hand the reverse phenomenon is expected from consideration of the hydrogen bonding forces. However, since the effective range of hydrogen bridges is limited to a distance of 2.5 Å, the inter- and intramolecular hydrogen bonding forces are expected to pass through a max with increasing coil size (12). It is evident from the summation of the two types of forces that the *resultant cohesive forces* pass through a max at an intermediate ethylene oxide chain length. Hence, the max resistance to film rupture at the CHHB or the corresponding max in foam stability at the CHHB is explained.

It is worth noting that differences in the CHHB values in the five homologous series also may be attributed to the summation of the two types of cohesive forces. The van der Waals' forces exerted by branched hydrophobic groups exceed those of straight chain homologs; the molar cohesion of the $-CH_3$ groups amounts to 1780 cal/mole compared to only 990 cal/mole for the$-CH_2$-group (12). Therefore, to obtain max cohesive forces a longer ethylene oxide chain is required in a comparison of two nonionic detergents with approx equal length of the straight chain part of the hydrophobic group to balance a branched hydrophobic group compared to a straight chain one. This is borne out by our results; the CHHB of the nonylphenol series is much higher, 2.9, than that of the n-dodecanol series, 0.6.

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[2] It is generally recognized that the solubility of poly(oxyethylene) compounds is affected by hydrogen bonding of water molecules by the ether oxygens.

ACKNOWLEDGMENT

Permission for publication granted by Lever Brothers Co.

REFERENCES

1. Mayhew, R. L., and R. C. Hyatt, JAOCS *29*, 357 (1952).
2. Shinoda, K., T. Yamanaka, and K. Kinoshita, J. Phys. Chem. *63*, 648 (1959).
3. Walling, C., E. E. Ruff, and J. L. Thornton, *Ibid. 56*, 989 (1952).
4. Corkill, J. M., J. F. Goodman, and R. H. Ottewill, Trans. Faraday Soc. *57*, 1627 (1961).
5. Flory,P. J., J. Am. Chem. Soc. *62*, 1561 (1940).
6. Schick,, M. J., J. Colloid Sci., *17*, 801 (1962).
7. DeVries, A. J., Recueil Des Travaux Chimiques Des Pays-Bas *77*, 81 (1958).
8. Kitchener, J. A., and C. F. Cooper, Quarterly Reviews, London; The Chemical Society *13*, 71 (1959).
9. Mysels, K. J., K. Shinoda, and S. Frankel, "Soap Films," Pergamon Press, New York (1959).
10. Brown, A. G., W. C. Thuman, and J. W. McBain, J. Colloid Sci. *8*, 491 (1953).
11. Miles, G. D., J. Ross, and L. Shedlovsky, JAOCS *27*, 268 (1950).
12. Mark, H., and A. V. Tobolsky, "Physical Chemistry of High Polymeric Systems," 2nd ed., Interscience Publishers, Inc., New York, 1950, pp. 133 and 144.

[Received August 27, 1962—Accepted October 30, 1962]