TABLE I

Analyses of Lipid Extracts

Fraction No.	% Oil of total	% Phosphatides Px25	I.V. (Wijs)	I.V. (GLC)	Fatty acid composition, % Myristic	Palmitic	Palmitoleic	Stearic	Oleic	Linoleic	Malvalic[a]
1	24.5	0.16	109.0	112.3	1.1	23.6	1.1	2.0	15.6	56.3	0.30
2	14.0	0.05	110.0	111.5	1.8	23.0	1.1	2.3	15.9	55.6	0.37
3	13.9	0.52	107.8	109.0	1.8	24.8	1.0	2.1	15.7	54.2	0.54
4	14.7	0.45	107.5	109.3	1.8	24.8	1.2	1.9	15.1	54.5	0.82
5	18.2	0.50	107.7	109.0	1.2	24.2	0.4	2.6	16.8	53.9	0.97
6	14.7	0.59	107.2	108.9	0.9	23.4	0.9	3.1	17.6	53.1	1.06
Whole oil[b]		0.41 (0.36)	109.0 (108.3)	111.1 (110.2)	1.2 (1.3)	23.3 (23.9)	1.0 (0.9)	2.3 (2.3)	16.5 (16.2)	55.0 (54.7)	0.64 (0.66)

[a] Determined by HBr titration.

[b] Values in parenthesis are weighted averages calculated from the individual fractions.

sary. The results also have morphological significance in that they indicate that the cyclopropenoid constituents are concd in specific areas of the seed which are not readily accessible to solvent.

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REFERENCES

1. Bailey, A. V., F. C. Magne, R. A. Pittman and E. L. Skau, JAOCS *38*, 505 (1961).
2. Harris, J. A., F. C. Magne and E. L. Skau, *Ibid. 41*, 309 (1964).
3. Pons, W. A., Jr., M. F. Stansbury and C. L. Hoffpauir, J. Assoc. Offic. Agr. Chemists *36*, 492 (1953).
4. Arnold, L. K., and B. R. Choudhury, JAOCS *38*, 87 (1961).
5. Bull, W. C., and T. H. Hopper, Oil Soap *18*, 219 (1941).

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The Effect of Temperature upon Foam Fractionation

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Abstract

An experimental investigation is presented of the effect of temp on the foam fractionation of the ethylhexadecyldimethylammonium bromide-water system. Two feed concn, two foam heights, and a temp range of 14–54C are included. For each fixed set of values of feed concn and of foam height, the greater and lesser coefficients of fractionation are both increasing functions of temp. The effect of a variation in temp on the greater coefficient is more pronounced for more dilute feed solutions, and at greater foam heights. The effect of a temp change on the lesser coefficient is more pronounced for more concd feed solutions and is not related to foam height. At any fixed temp, an increase in feed concn at constant foam height generally decreases the greater coefficient and decreases the lesser coefficient. An increase in foam height at constant feed concn increases both coefficients. The greater and lesser coefficients may be related to temp by power equations with 5% accuracy. The above results may be explained qualitatively on the basis of the response of foam stability and drainage to temp.

Introduction

FOAM FRACTIONATION has been utilized by chemists, biochemists and engineers for the separation of organic and inorganic materials from dilute aqueous solutions. Applications of the process include the separation of enzymes, the transfer of organic solutes which by themselves have little foaming ability, the removal of radioactive metal ions from waste streams and the treatment of secondary sewage effluents for the separation of non-biodegradable organics. Several extensive reviews of the process have appeared in the literature (1,11,12). Recently, a number of studies have been made on the operating and system variables affecting the process. Grieves et al. have determined the influence of foam height and foam column diam (7), the influence of surfactant, feed concn, air rate and feed rate (5,6,8), the effect of liquid solution height (7,8) and the effect of feed position (5,8) upon the continuous foam fractionation of anionic and cationic surfactants. Other studies of this nature have been conducted by Kevorkian (9), by Kishimoto (10) and by Brunner and Lemlich (2).

The information available on the influence of temp on the process is very limited. Grieves and Wood (8) studied variations with temp of the continuous foam fractionation of ethylhexadecyldimethylammonium bromide solutions, but their temp range was limited to 24–38C. Kishimoto (10) reported the effect of temp upon the batch foaming of sodium lauryl sulfate solutions, but his temp range was limited to 10–22C. Bikerman (1) has reviewed a number of investigations concerned with the relation between foam stability and temp; however, none of these studies were concerned with foam fractionation. The overall objective of this investigation is the establishment of the influence of temp upon the greater and lesser coefficients of fractionation for the ethylhexadecyldimethylammonium bromide-water (EHDA-Br) system. Two feed concn, two foam heights and a broad range of temp are included in the experiments.

Experimental

All of the experiments were conducted in a 10-cm diam, 105 cm high, cylindrical column, made of lucite. High-purity nitrogen was saturated with water, metered with a calibrated rotameter, and passed through twin, 50 μ, fritted-glass diffusers. In each experiment, 2000 ml of the feed solution of EHDA-Br in distilled water were placed in the column. Nitrogen bubbles were dispersed through the solution for a period of 15 min with continuous foam removal at a port located at a selected height above the feed solution level. Feed concn of 87.5 mg/liter (2.31×10^{-4} M) and 125 mg/liter (3.30×10^{-4} M) were employed, with a nitrogen rate of 4950 ml/min (at Standard Temperature and Pressure) used with the 87.5 mg/liter solutions and of 3700 ml/min (STP) used with the 125 mg/liter solutions. Foam was removed at heights of 15.2 cm and of 77.8 cm above the average bulk solution level during the experiments. The temp of the solution and of the foam at the point of foam removal were measured to the nearest 0.5C throughout each run, and an average operating temp was computed. At the termination of each experiment the residual solution volume was measured and the concn of EHDA-Br

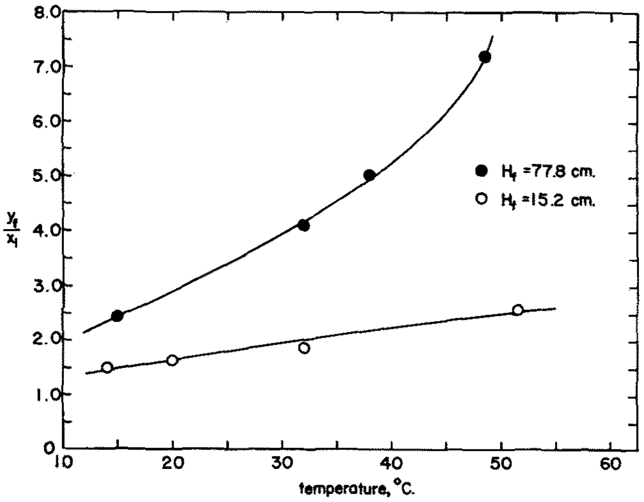

FIG. 1. Relationships between the greater coefficient of fractionation and temp for 87.5 mg/liter feed solutions.

was determined by a two phase titration technique (3). Random analyses of the collapsed foam were conducted for material balance verification. The analyses were accurate to within ±1.0 mg/liter.

Results and Discussion

Results of the experiments are presented in Figures 1–4 in which the greater and lesser coefficients of fractionation are related to temp. Temp investigated ranged from 14–54C. The greater coefficient is defined as y_f/x_i and the lesser coefficient as x_r/x_i, in which x_i (mg/liter) is the concn of EHDA-Br in the feed solution, and y_f and x_r are the concn in the collapsed foam and residual solution, respectively. For each experiment, the following material balances may be written:

$$V_i = V_r + V_f \quad [1]$$

$$x_iV_i = x_rV_r + y_fV_f \quad [2]$$

V_i, V_r and V_f are the volumes in ml of feed solution, residual solution and collapsed foam, respectively. V_i was held constant at 2000 ml. For given x_i and V_i, y_f may be computed from experimental values of x_r and V_r, using Equations 1 and 2.

Figure 1 shows the effect of temp on the greater coefficient for 87.5 mg/liter feed solutions, with parameters of foam height (H_f, cm). Figure 2 presents similar relations for 125 mg/liter feed solutions. For each fixed set of values of x_i and H_f (i.e., for each curve), an increase in temp always provides an increase in the greater coefficient of fractionation. The effect of a variation in temp, $[(x_r/x_i) @ t_1/(x_r/x_i) @ t_2]$, is most pronounced for $x_i = 87.5$ mg/liter and $H_f = 77.8$ cm. For constant x_i, the influence of a variation in temp is always greater at the larger foam height, particularly at higher temp. The slopes of the y_f/x_i vs. temp curves sharply increase at high temp for $H_f = 77.8$ cm, while they tend to decrease slightly or become constant for $H_f = 15.2$ cm. Comparing results for both feed concn (at constant H_f), the effect of temp variation is greater for the more dilute feed solutions, but only at $H_f = 77.8$ cm. At $H_f = 15.2$ cm, the effect is minimal; however some of the response may have been shielded by the higher nitrogen flow rate that was used with the more dilute solutions. It has been shown previously (5) that an increase in gas rate with all other variables held constant provides a less rich foam. Considering both figures, at 15C y_f/x_i ranges from 1.41–2.44, while at 48.5C y_f/x_i ranges from 2.43–7.21. Thus at higher temp, variations in feed concn and foam height have a more marked influence on the greater coefficient of fractionation.

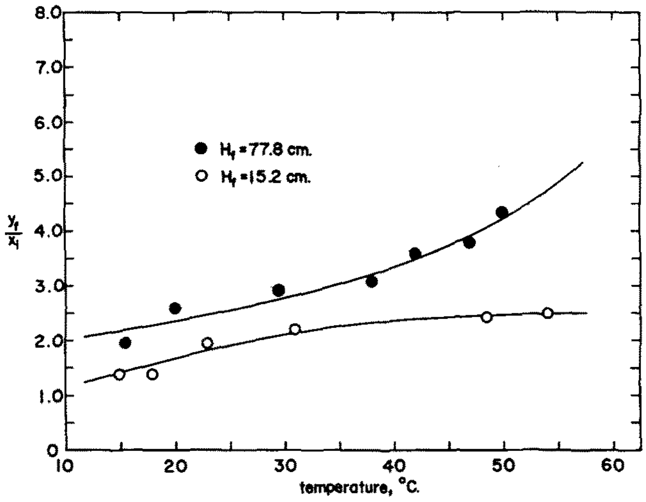

FIG. 2. Relationships between the greater coefficient of fractionation and temp for 125 mg/liter feed solutions.

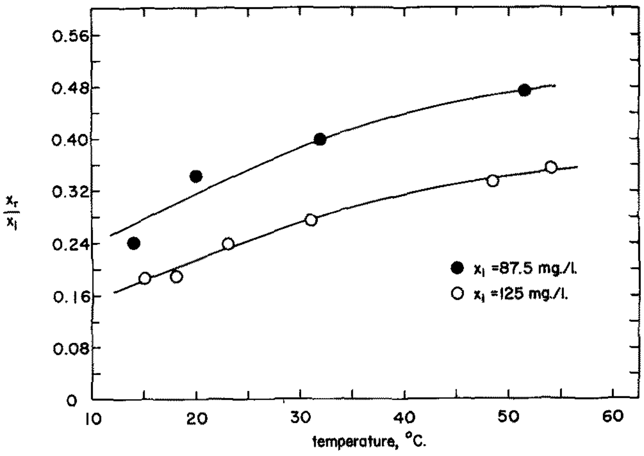

FIG. 3. Relationships between the lesser coefficient of fractionation and temp for a foam height of 15.2 cm.

Figure 3 presents the variation of the lesser coefficient with temp for a foam height of 15.2 cm; the parameters are feed concn. Figure 4 shows similar relations for a foam height of 77.8 cm. For each fixed set of values of x_i and H_f, an increase in temp always brings about an increase in the lesser coefficient. For any fixed temp, an increase in x_i decreases x_r/x_i (at constant H_f), which is more pronounced

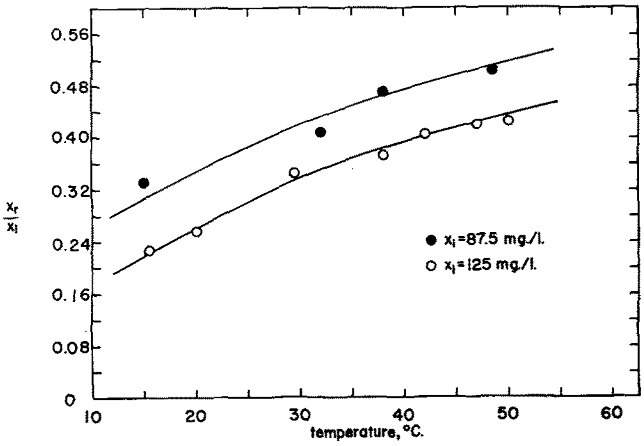

FIG. 4. Relationships between the lesser coefficient of fractionation and temp for a foam height of 77.8 cm.

TABLE I

Values of Constants in Equations for Greater and Lesser Coefficients

$y_f/x_i = k_1\ (t)^{n_1}$

x_i, mg/liter	H_f, cm	k_1	n_1
87.5	15.2	0.500	0.398
87.5	77.8	0.170	0.947
125	15.2	0.500	0.398
125	77.8	0.139	0.565

$x_r/x_i = k_2\ (t)^{n_2}$

x_i, mg/liter	H_f, cm	k_2	n_2
87.5	15.2	0.113	0.360
87.5	77.8	0.122	0.362
125	15.2	0.048	0.502
125	77.8	0.060	0.505

at $H_f = 15.2$ cm. For any fixed temp, an increase in H_f raises x_r/x_i (at constant x_i) and this is more marked at $x_i = 125$ mg/liter.

The data for the greater and lesser coefficients of fractionation can be related to temp analytically. The best fit for all of the points was provided by power equations of the following form:

$$y_f/x_i = k_1\ (t)^{n_1} \qquad [3]$$

$$x_r/x_i = k_2\ (t)^{n_2} \qquad [4]$$

in which k_1, n_1, k_2 and n_2 are constants. Values of the constants for each feed concn and foam height are given in Table I. It may be observed that the effect of a variation in temp upon the lesser coefficient at constant feed concn is independent of foam height, as shown by the values of n_2. But at constant foam height, the effect is a function of x_i and is more pronounced at $x_i = 125$ mg/liter.

This is in direct contrast to the behavior of the greater coefficient. In general, the sensitivity of the greater coefficient to temp is more marked than the lesser coefficient. The average percentage deviation of values of the greater coefficients calculated with Equations 3 and 4 and Table I from experimental values is 6.52%. Similar calculations for the lesser coefficient provides an average deviation of 3.51%. (Average percentage deviation:

$$\frac{|\,\text{experimental} - \text{calculated}\,|}{\text{experimental}} \times 100).$$

The coefficients of fractionation obtained in this investigation are functions of two factors: the tendency of the unsymmetrical EHDA-Br molecules to accumulate at the gas-liquid interfaces associated with the nitrogen bubbles; and the stability and drainage of the foam phase rising above the bulk solution. The first factor is partly described by Gibbs' Equation, which for dilute solutions may be written as follows:

$$\Gamma = -\frac{c}{RT}\frac{d\gamma}{dc} \qquad [5]$$

Γ is the excess number of moles of EHDA-Br/cm² of gas-liquid interface over the number of moles of EHDA-Br in that quantity of bulk solution containing the same number of moles of water as the interface; c is the bulk solution concn in g mole/ml; R is the gas constant in dyne cm/g mole °K; T is the absolute temp in °K; and γ is the surface tension of the bulk solution in dyne/cm. For the surfactant and the range of concn studied, surface tension was found to be virtually independent of temp. The surface tension of 125 mg/liter solutions varied from 45.1–47.1 dyne/cm in a random manner for temp from 8–51C. For 87.5 mg/liter solutions, the variation was from 49.7–50.2 dyne/cm. Thus, according to Equation 5 the surface excess is inversely proportional to the absolute temp, and seemingly the greater coefficient of fractionation should be a similar function.

In this regard, two additional points should be noted. First, it has been shown by Grieves and Bhattacharyya (4) and by Kishimoto (10) that an important factor influencing the concn of the foam stream is the amt of entrained, bulk solution carried up mechanically with the foam; foam drainage then becomes a most significant variable. Second, in addition to the single transfer stage in the bulk solution, multiple stages exist in the rising column of foam, and each cross-section of foam is enriched continually by the drainage of concd liquid from the foam layers above the particular cross-section. Multiple stages do not exist in a continuous process (4) but are a significant factor in a batch process since the concn of EHDA-Br in the foam and thus in the draining liquid continually decreases with time. The Gibbs Equation may be applied to each stage, but the number of stages is a function of foam stability and drainage.

Foam stability is generally a decreasing function of temp (1), while foam drainage is invariably an increasing function of temp. Both of these properties depend largely upon the viscosity and/or surface viscosity of the liquid in the foam phase, and for such solutions viscosity is an inverse function of temp. Elevation of temp thus could result in an increase in the greater coefficient of fractionation in spite of Gibbs' Equation, due to the drainage of more entrained liquid from the foam and due to the establishment of more transfer stages in the foam. This effect would be more pronounced for greater foam heights and for more dilute solutions. The latter would be caused by the greater sensitivity to temp of the thinner surfactant films in the foam phase formed from more dilute solutions. However, the influence of decreasing the feed concn would be lessened by the higher gas rate employed; an increase in gas rate would produce more entrained liquid and a less rich foam. The increase of the lesser coefficient with temp would be brought about by more EHDA-Br returning to the residual solution due to foam drainage and instability. As the magnitude of the collapsed foam volume decreases and the foam becomes richer, the concn of the residual solution must increase since a greater volume of concd liquid is draining.

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REFERENCES

1. Bikerman, J. J., "Foams: Theory and Industrial Applications," 1st ed., Reinhold Publishing Corp., New York, 1953.
2. Brunner, C. A., and R. Lemlich, Ind. Eng. Chem. (Fundamentals) *2*, 297–300 (1963).
3. Edwards, G. P., and M. E. Ginn, Sewage Ind. Wastes *26*, 945–952 (1954).
4. Grieves, R. B., and D. Bhattacharyya, J. Water Pollution Control Federation (in press).
5. Grieves, R. B., C. J. Crandall and R. K. Wood, Int. Journal Air Water Pollution, 8, 501–513 (1964).
6. Grieves, R. B., S. Kelman, W. R. Obermann and R. K. Wood, Canad. J. Chem. Eng. *41*, 252–257 (1963).
7. Grieves, R. B., and R. K. Wood, Nature *200*, 332–335 (1963).
8. Grieves, R. B., and R. K. Wood, A.I.Ch.E. Journal, 10, 456–460 (1964).
9. Kevorkian, V., Ph.D. thesis, Columbia Univ., New York, 1958.
10. Kishimoto, H., Kolloid-Z. *192*, 66–101 (1963).
11. Kobe, K. A., and J. J. McKetta, Ed., "Advances in Petroleum Chemistry and Refining," 1st ed., Vol. 7, John Wiley & Sons, New York, 1962, pp. 66–135.
12. Schoen, H. M., Ed., "New Chemical Engineering Separation Techniques," 1st ed., *Ibid.* pp. 319–385.

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