Foam Fractionation of Colloid-Surfactant Systems

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The presence of colloidal particulates has a significant effect upon the foam fractionation of aqueous solutions of surface-active agents. An experimental investigation is presented of the foam fractionation-flotation of the stannic oxide-cetyltrimethylammonium bromide (CTAB) and stannic oxide-alkyl benzene sulfonate (ABS) systems. The average diameter of the stannic oxide particles was 180Å, and particle concentrations were determined by turbidimetry. For stannic oxide-CTAB a froth flotation mechanism controls, and upon foaming feed sols of fixed concentration, fractional residuals of particulates and surfactant are approximately equal. Maximum enrichment ratios are obtained at maximum aeration time, minimum air rate, and maximum foam height. Increasing the feed concentration of particulates increases the collapsed foam volume, while the CTAB concentration in the residual sol first decreases and then becomes virtually constant. For stannic oxide-ABS sols, no particulates are removed preferentially in the foam. A foam fractionation mechanism controls, and compared with ABS solutions the addition of stannic oxide decreases the foam volume and residual ABS concentration, producing a pronounced increase in the enrichment ratio.

In addition to various chemical and biological separations, foam fractionation has been used successfully in a number of engineering applications (*11, 15*). Radioactive metal ions have been separated from aqueous solutions by the addition of surface-active agents which complex with the ions and carry them into the foam stream (*16*). Alkyl benzene sulfonate and organics analyzed as chemical oxygen demand have been foam fractionated from secondary sewage effluents (*14*). Foam fractionation employs the tendency of unsymmetrical organic molecules to accumulate at the air-aqueous solution interfaces associated with generated bubbles. The process deals with a homogeneous system in contrast to froth flotation which deals with a heterogeneous system involving a liquid phase and one or more solid phases. Froth flotation relies on the selective production of hydrocarbonlike surfaces on nonhydrocarbon particles which are floated to the surface of the aqueous system by aeration and bubble attachment.

Of the vast amount of work reported in the literature on froth flotation (*15, 18*), only a small fraction has been concerned wih colloidal size particulates. Studies have been conducted by Clanton et al. (*3, 12*) on ferric oxide, aluminum oxide, and chromic oxide, and an extensive investigation of silver iodide has been carried out by Jaycock and Ottewill (*9*). Fundamental interest has been centered on the colloidal particulates and not on the surface-active collectors, their separation into the foam, or on foam stability. Of the numerous variables which have been studied in connection with the foam fractionation process, the effect of the presence of colloidal size particulates has been totally neglected. The existence of such particles in a process or waste stream should have a most pronounced effect on the separation of surfactants. It is quite possible that the process could be extended to the removal of weakly surface-active organics by the addition of particles and by the establishment of a froth flotation mechanism.

The objective of this investigation is the establishment of the influence of hydrophobic, negatively charged, colloidal particulates upon the batch foam fractionation of aqueous solutions of cationic and anionic surfactants. This will include the effect of particle concentration, surfactant concentration, air rate, aeration time, and foam height upon the removal of both surfactant and particulates from the feed sols.

EXPERIMENTAL

A negatively charged, stannic oxide sol was prepared by reacting 20 g. of sodium stannate with 180 ml. of 1.0 N sulfuric acid in boiling water. The precipitate was permitted to settle, and the decanted solution was replaced three times with fresh water. Peptization was carried out by the addition of 40 ml. of 1.6 N ammonium hydroxide followed by boiling to remove the excess ammonia. The sol was diluted to give a sol containing 2,000 mg./liter of stannic oxide, which was utilized in most of the experiments. The pH of the diluted sol was 7.4. Demineralized water was used in all of the preparation steps. Electron micrographs were taken of the sol, which indicated an approximately monodisperse suspension of spherical particles, 180Å in diameter. Thus, the specific surface of the sol particles was approximately 1.2×10^5 sq.cm./g., and, with a density of 7.0 g./cc. assumed, there were approximately 10^{14} particles per milliliter of sol.

Three series of experiments were carried out. The first employed feed sols containing 2,000 mg./liter of freshly prepared stannic oxide and 50 mg./liter (1.37×10^{-4} M.) cetyltrimethylammonium bromide, a cationic surfactant. In the second series feed concentrations of stannic oxide were varied from 850 to 3,000 mg./liter and of CTAB from 30 to 70 mg./liter. In the third, the feed sols contained 2,000 mg./liter of stannic oxide and 47.9 mg./liter (1.37×10^{-4} M.) alkyl benzene sulfonate, an anionic surfactant. All of the foam studies were carried out in a 10-cm. diameter, 130 cm. high, Lucite cylindrical column. Filtered, saturated air was metered by a rotameter and passed through a 3.8-cm. diameter, 35 μ porous metal diffuser. In each experiment, the temperature was controlled at 23°C., and 800 ml. of feed sol were foamed. The foam was passed into a receiver and was collapsed thermally; no collapsed foam was returned to the column. Aeration times were varied from 2 to 15 min., air rates from 2,320 to 11,460 ml./min. (at 25°C. and 1.0 lb./sq. in. gauge), and the heights of foam removal (height of column of foam) above the initial feed solution level in the column from 12 to 114 cm. After the completion of each run, the volumes of collapsed foam and residual sol were measured, and the foam and residual sol were analyzed for surfactant concentrations. CTAB and ABS concentrations were determined by a two-phase titration technique (*4*) and were accurate to ± 0.6 mg./liter.

TURBIDIMETRY

Concentrations of stannic oxide particulates in the residual sols were determined by turbidity measurements in a spectrophotometer, with a wave length of incident light of 5,000Å. Optical density (turbidity) is the measure of the decrease in light beam intensity due to scattering as it passes through the sample (*1*):

$$I = I_o\, e^{-Tl} \qquad (1)$$

For small, isotropic particles of radius less than 1/20 the wave length of the incident light, in the absence of consumptive light absorption, the turbidity may be related to the number of particles per milliliter and to their individual volume by Rayleigh's equation (*13*):

$$T = A N V^2 \qquad (2)$$

A is an optical constant and a function of the wave length of the incident light, the refractive index of the solvent, and the refractive index of the particles.

The turbidity of the 2,000 mg./liter feed sols used in the first and third series of experiments was 0.16. Dilution of the sol with demineralized water gave the linear relation shown in the lower part of Figure 1, in which T is related to the reciprocal of the sol volume obtained by diluting an original 50-ml. sample. Linearity could be predicted from Equation (2) since, for constant particle size, T is directly proportional to the number of particles present in the sample. Upon the addition of 2.5 mg. of CTAB to a 50-ml. sol sample, (50 mg./liter), a rise in turbidity from 0.16 to 0.31 was noted. This was caused by adsorption of CTAB on the stannic oxide particulates and by the resulting partial coagulation of the particles into aggregates. Thus the number of particles was reduced and the volume per particle was increased, and Equation (2) predicts a rise in turbidity. (The turbidity of a 50 mg./liter solution of CTAB was zero, indicating no light absorption.)

This behavior is analogous to that of silver iodide sols upon the addition of cationic surfactants (*10, 13*). The first step involves the electrostatic attraction of CTAB cations in the Stern layers at the negatively charged surfaces of the stannic oxide particulates. The surfactant cations are oriented with the head groups in which the positive charge is centralized pointing toward the particle and with the hydrocarbon chains (cetyl or hexadecyl groups) orthagonal to the particle surface or lying flat along the surface. The second step involves the partial coagulation or aggregation of the oleophilic particulates promoted by van der Waals attractive forces between the hydrocarbon chains. The addition of larger concentrations of CTAB (above 50 mg./liter) should bring about complete coagulation of the sol, corresponding to the zero point of charge. Approximately 95 mg./liter of CTAB were required to coagulate completely 2,000 mg./liter of stannic oxide. Higher concentrations should cause charge reversal.

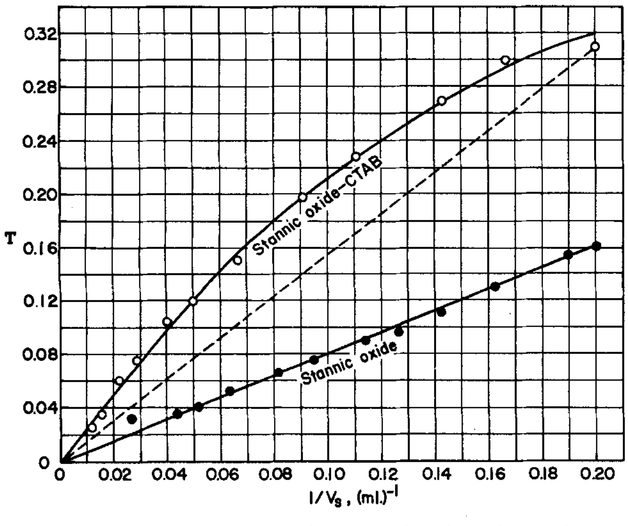

Fig. 1. Turbidity of diluted sols vs. sample volume (inverse).

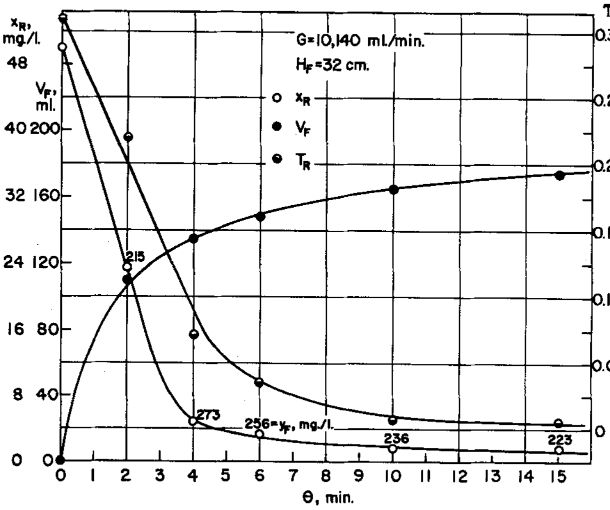

Fig. 2. Relations between V_F, x_R, T_R, and θ for stannic oxide-CTAB sols.

Dilution of the sol containing CTAB (50 mg./liter) and stannic oxide (2,000 mg./liter) did not give a linear relation (light-dotted line), as indicated by the upper curve in Figure 1. More dilute sols gave higher turbidities than the linear relation woud predict. It can be hypothesized that this behavior was caused by the splitting off of a limited number of individual particulates from the large aggregates due to desorption of CTAB in the more dilute solutions. This would cause the presence of more particles and more scattering, without significantly decreasing the scattering caused by the aggregates.

STANNIC OXIDE-CTAB SYSTEM: EFFECT OF OPERATING VARIABLES

The first series of experiments involved the effect of aeration time, air rate, and foam height upon the foam fractionation-flotation of the stannic oxide-CTAB system. Figure 2 relates collapsed foam volume (feed sol volume = 800 ml.), concentration of CTAB in the residual sol, and turbidity of the residual sol to aeration time. Each of the experiments was conducted with an air rate of 10,140 ml./min. and with foam removal 32 cm. above the initial feed sol level. For each point on the $x_R - \Theta$ curve, the CTAB concentration in the collapsed foam y_F is given. Virtually all of the separation was obtained in the first six minutes of foaming. During this period the accumulative concentration of CTAB in the collapsed foam passed through a maximum. Beyond 6 min. a small amount of rather dilute foam was produced. A maximum value of the enrichment ratio $y_F/x_R = 150$ was obtained at $\Theta = 10$ min. The similar behavior of the $x_R - \Theta$ and $T_R - \Theta$ curves should be noted. T_R is a measure of the particulates remaining in the residual solution and is discussed below.

Figure 3 presents the results of experiments involving the effect of air rate and foam height. V_F, x_R, and T_R are related to air rate G with parameters of H_F, the height of foam removal above the liquid level of the feed sol. The initial liquid level of the feed sol was always 10 cm. above the column base. Numerical values for y_F are again

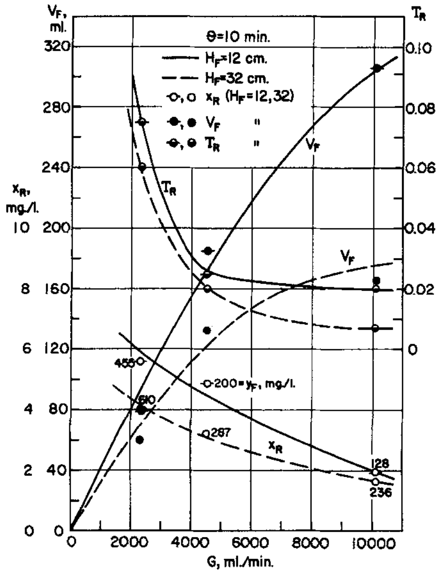

Fig. 3. Relations between V_F, x_R, T_R, and G for stannic oxide-CTAB sols (parameters: H_F).

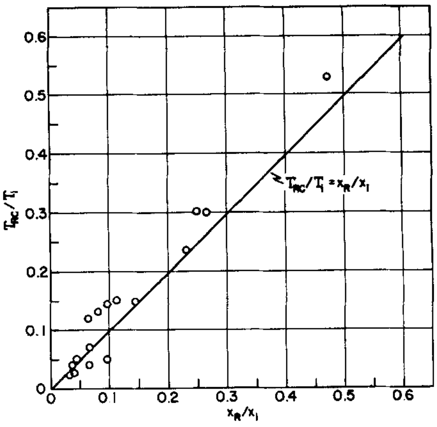

Fig. 4. Relation between fractional residuals of stannic oxide and of CTAB.

given. All of the runs were made with a 10 min. aeration time. An increase in air rate at constant foam height provided a greater foam volume and lower concentrations of CTAB and particulates in the residual sol; however, as G was increased, the collapsed foam concentration decreased, and the richest foam (both in CTAB and in particulates) was obtained at the lowest air rate. This behavior is analogous to that observed by Grieves et al. (*7*) on the foam separation of pure surfactant solutions. An increase in air rate provided an increase in interfacial area to which more particles became attached; however, as more particles were carried into the foam, more bulk sol was mechanically entrained, only a fraction of which drained, and thus the foam was diluted. An increase in the height of foam removal permitted longer drainage times for the foam and produced higher values of the collapsed foam concentration at all air rates. In addition, lower values of x_R were obtained at the higher value of H_F. This indicated that further enrichment and particle attachment to the gas liquid interfaces associated with the bubbles occurred in the foam as it rose above the solution. The entrained sol that drained from the foam became more dilute as the foam was permitted to rise to a greater height. Apparently, equilibrium was not established in the solution which is in direct contrast to behavior noted for pure surfactant solutions (*6, 8*).

It may be observed that although the $x_R - G$ and $T_R - G$ curves indicated similar removals at a given G and H_F, T_R/T_i and x_R/x_i were not the same, but T_R/T_i was always greater than x_R/x_i. This may be explained on the basis that T_R is an inaccurate measure of the residual particle concentration in the sol. During the actual foaming process, as the residual solution became more dilute, individual particles could break away from the aggregates, and the resulting turbidity would be higher than that obtained for constant particle size. It can be postulated that the turbidity of the sol during the foaming process decreased along the upper dilution curve in Figure 1, and thus that a greater fraction of particles was removed than T_R would indicate. The volume of sol carried into the foam during the course of the foaming process and the dilution volume plotted on the abscissa of Figure 1 are, of course, in no way related.

The dilution curve can be used to convert residual turbidities into more adequate measures of the total number of particles (or weight of stannic oxide) in the residual sol. For a total of sixteen experiments conducted with identical feed sols but foamed under different operating conditions, the T_R values were converted into cor-

TABLE 1. COMPARISONS BETWEEN CTAB AND ABS SOLUTIONS AND SOLS

	CTAB (x_i = 50.0 mg./liter)	CTAB + Stannic oxide (x_i = 50.0 mg./liter)	ABS (x_i = 47.9 mg./liter)	ABS + Stannic oxide (x_i = 47.9 mg./liter)
(Θ = 10 min., G = 2320 ml./min., H_F = 12 cm.)				
V_F, ml. (V_i = 800 ml.)	0	79	541	300
x_R, mg./liter	50.0	5.6	5.5	2.5
y_F, mg./liter	—	455	68	123
(Θ = 10 min., G = 2320 ml./min., H_F = 32 cm.)				
V_F, ml. (V_i = 800 ml.)	0	60	315	132
x_R, mg./liter	50.0	4.0	7.5	3.1
y_F, mg./liter	—	610	110	274
(Θ = 10 min., G = 10140 ml./min., H_F = 12 cm.)				
V_F, ml. (V_i = 800 ml.)	27	306	800	—
x_R, mg./liter	40.4	1.9	—	—
y_F, mg./liter	330	128	47.9	—

rected turbidities T_{RC} by using the dotted line (theoretical linear relation, with Rayleigh's equation assumed) and curve in the upper part of Figure 1. For example, $T_R = 0.22$ yielded $T_{RC} = 0.16$, at the same abscissa value, thus taking into account the higher turbidity resulting from individual particles breaking away from the aggregates. Figure 4 relates T_{RC}/T_i to x_R/x_i, and reasonable agreement is obtained between the fractional residuals of stannic oxide and CTAB. Since preliminary adsorption of CTAB on the particulates was essential for the flotation of the stannic oxide, and as long as significant desorption did not take place during the course of an experiment, such agreement would be expected. For this series of experiments, approximately 830 molecules of CTAB were removed with each particle of stannic oxide.

Comparisons are presented in Table 1 between experiments conducted with stannic oxide-CTAB sols and with pure solutions of CTAB, under identical operating conditions. The foaming properties of CTAB were changed vastly by the presence of the colloidal particulates. For pure CTAB at the low air rate, no foam was produced. At the high air rate there was some foaming and a true foam fractionation mechanism occurred, with foam formation and the separation obtained depending upon the tendency of the CTAB molecules to migrate to the interfaces associated with the bubbles. For CTAB and stannic oxide, much larger quantities of foam were produced (than for pure CTAB) and a froth flotation mechanism occurred, with the particulates, made oleophilic and aggregated by the CTAB, attaching to the bubbles and being lifted into the foam phase. Foam stability primarily depends upon the noncoalescence of bubbles and in accordance with Bikerman (2) is strongly enhanced by the presence of particulates in contact with air bubbles. The effect of stannic oxide upon the stability of CTAB foams is clearly shown in Table 1. The addition of 2,000 mg./liter of stannic oxide to 50 mg./liter of CTAB had a small effect upon surface tension, raising it from 60 to 62 dynes/cm.

STANNIC OXIDE-CTAB SYSTEM: EFFECT OF CONCENTRATION

A second series of experiments was conducted to establish the influence of surfactant and particulate concentrations upon the foam fractionation-flotation of the stannic oxide-CTAB system. Figure 5 relates V_F and x_R to T_i, with parameters of x_i. All of the runs were made with an aeration time of 4 min., an air rate of 11,460 ml./min., and a foam height of 62 cm. For constant x_i, increasing T_i increased V_F, while x_R at first significantly decreased and then became relatively constant. It appears likely that below a certain critical value of T_i the number of particulates floated was limited by the number of particulates present in the feed sol. Thus, a rise in T_i decreased x_R since, although the amount of CTAB adsorbed on each particle decreased, virtually all of the added particulates were floated and more CTAB was preferentially carried into the foam. Above the critical value of T_i, approximately 0.11, the addition of more particles had little effect upon x_R, since the process became limited by the number of bubbles. A reduced fraction of the added particles was floated owing to bubble saturation, while the amount of CTAB adsorbed per particle continued to decrease. Above the critical T_i, V_F still continued to increase with T_i since more particles were floated (with less surfactant per particle) and foam stability and drainage are strong functions of the particulate concentration in the foam. In all cases the richest foams were obtained at the lowest values of T_i, indicating that the presence of more particulates in the foam decreased foam drainage, and less of the entrained sol was able to drain from the foam.

For constant T_i, increasing x_i increased V_F and provided a richer foam. For greater values of x_i, more CTAB was adsorbed per particle, making each particle more oleophilic and thus carrying a larger fraction of particles and CTAB into the foam phase.

STANNIC OXIDE-ABS SYSTEM

A final series of experiments was carried out utilizing sols containing 2,000 mg./liter of stannic oxide and 47.9 mg./liter of alkyl benzene sulfonate, an anionic surfactant. Comparative runs were made with 47.9 mg./liter solutions of pure ABS. The addition of ABS to the negatively charged stannic oxide sol resulted in no partial coagulation (formation of aggregates), which was indicated by no increase in the turbidity of the sol. This behavior was expected, since the particulates and surfactant were both of the same charge and there was no electrostatic attraction, but rather repulsion, between the negatively charged surfaces and the ABS anions. In all of the experiments T_R was identical to T_i, and no particulates were preferentially removed in the foam. Stannic oxide particles lowered the surface tension of the pure ABS solutions from 59.5 to 56.6 dynes/cm.

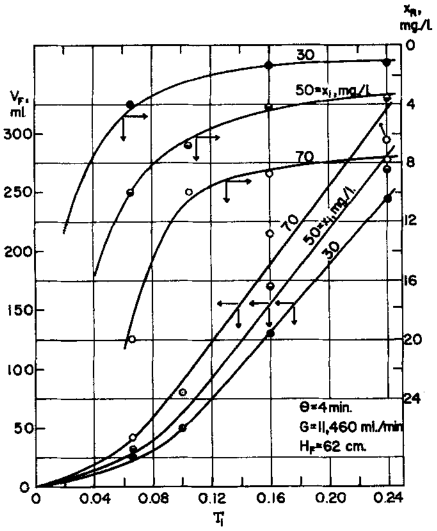

Fig. 5. Relations between V_F, x_R, and T_i for stannic oxide-CTAB sols (parameters: x_i).

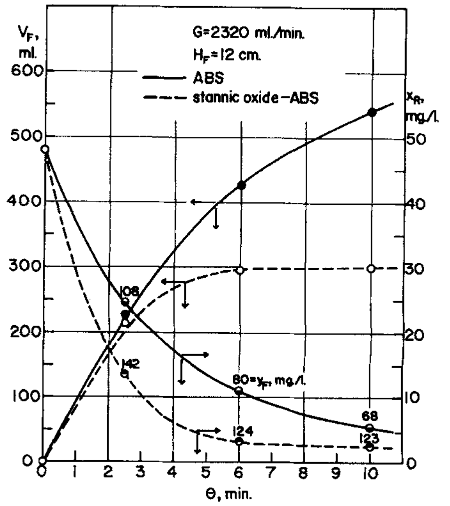

Fig. 6. Relations between V_F, x_R, and θ for ABS solutions and stannic oxide-ABS sols.

Figure 6 relates the volume of collapsed foam and residual ABS concentration to aeration time for pure ABS solutions and for stannic oxide-ABS sols. Numerical values of the concentrations of collapsed foam are given. All of the experiments were conducted at an air rate of 2,320 ml./min. and foam height of 12 cm. In all cases foaming of the sols yielded lower values of both V_F and x_R and higher values of y_F than comparative runs with solutions. In contrast to the previous series of experiments, a true foam fractionation mechanism operated. The decrease in the values of V_F was caused by enhanced foam drainage and lessened foam stability owing to the presence of stannic oxide. The particulates could be considered as macroanions, and their effect is similar to that of chloride and sulfate ions on the continuous foam separation of ABS (*17*).

Data indicating the influence of foam height upon the volume and concentration of the foam formed from ABS solutions and stannic oxide-ABS sols are presented in Figure 7. Numerical values of x_R are given. The effects of the stannic oxide were the same as shown in Figure 6, except they became most pronounced at the largest value of H_F. At $H_F = 114$ cm. an enrichment ratio (y_F/x_R) of 383 was obtained with the sol, compared with a value of 25 for the ABS solution. These results would be expected, since the influence of the particulates on the migration of ABS ions, on foam drainage, and on foam stability should be maximized with a high column of foam.

Some comparative values for ABS solutions and stannic oxide-ABS sols, at the same feed concentrations and operating conditions as CTAB solutions and stannic oxide-CTAB sols, are given in Table 1. The extensive differences in foamability of the two surfactants and in the effect of stannic oxide upon the two are clearly shown. Stannic oxide increases the foamability of CTAB and improves the separations obtained; it decreases the foamability of ABS but improves the separations obtained.

CONCLUSIONS

An experimental investigation has been carried out of the foam fractionation-flotation of the stannic oxide-cetyltrimethyl ammonium bromide and stannic oxide-alkyl benzene sulfonate systems. For stannic oxide-CTAB sols in which the colloidal particles and surfactant have opposite charges, the CTAB cations are adsorbed on the colloid making it oleophilic and causing partial coagulation. Upon foaming, a froth flotation mechanism operates, and for fixed stannic oxide and CTAB concentrations in the feed sols, the fractional residuals of particulates and surfactant are approximately equal. Maximum enrichment ratios are obtained at maximum aeration time, minimum air rate, and maximum foam height. Increasing the feed concentration of particulates raises the collapsed foam volume, while the CTAB concentration in the residual sol first decreases and then becomes practically constant.

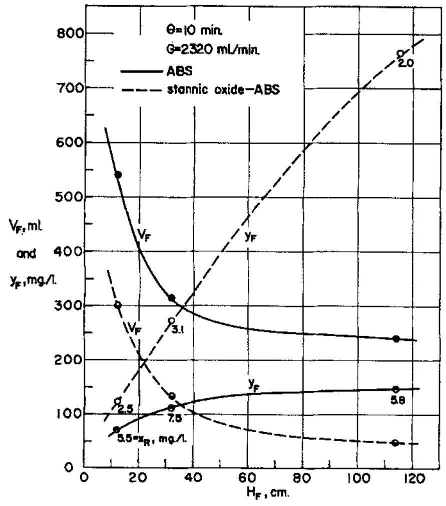

Fig. 7. Relations between V_F, y_F, and H_F for ABS solutions and stannic oxide-ABS sols.

For stannic oxide-ABS sols in which the particles and surfactant are of the same charge, no particulates are preferentially removed in the foam. A foam fractionation mechanism operates, and, compared with ABS solutions, the addition of stannic oxide decreases the foam volume and residual ABS concentration, producing a pronounced increase in the enrichment ratio.

The presence of colloidal size particulates has an important effect on the foam fractionation process, including the replacement of the foam fractionation mechanism by a froth flotation mechanism. The presence and charge of particles must be taken into account before subjecting a process or waste stream to foaming. Colloidal particulates appear to have some promise as additives to promote the removal of weakly surface-active organics from aqueous solutions.

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NOTATION

G = air rate, ml./min. (at 25°C. and 1.0 lb./sq. in. gauge)
H_F = height of column of foam above liquid level of feed sol, cm.
I = intensity of attenuated light beam, $(\text{sq. cm.})^{-1}$ sec.^{-1}
I_o = intensity of incident light beam, $(\text{sq. cm.})^{-1}$ sec.^{-1}
l = path length, cm.
N = number of particles per milliliter of sol
V = volume of a sol particle, cc.
V_F = volume of collapsed foam, ml.
V_S = volume of diluted sol sample, ml.
x_i = surfactant concentration in feed sol, mg./liter
x_R = surfactant concentration in residual sol or solution, mg./liter
y_F = surfactant concentration in collapsed foam, mg./liter
T = turbidity (optical density) [Equation (1)]
T_i = turbidity of feed sol
T_R = turbidity of residual sol
T_{RC} = corrected turbidity of residual sol
Θ = aeration time, min.

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Effect of Packing on the Catalytic Isomerization of Cyclopropane in Fixed and Fluidized Beds

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An experimental study with fixed and fluidized beds in the isomerization of cyclopropane on a silica alumina catalyst is reported for a temperature range of 150° to 250°C. and of 5 to 150 *W/F* (g-catalyst, hr./g.-mole). The effects of various cylindrical screen packing, 0.2-, 0.4-, and 1.0-in. diameter, and 1.0-in. diameter pall ring, on final conversion were determined. Reactor scale effects were also considered with reactors of 0.9-, 1.8-, and 6.0-in. diameter and bed heights 1.8 to 11.0 in.

Overall conversions were higher in a fluidized bed with packing than in a normal fluidized bed but were less than in a fixed bed, though approaching it in some cases. Rate data from the fixed bed closely followed first-order kinetics. When the same catalyst was tested in a normal fluidized bed, the rate was dependent on linear gas velocity and catalyst bed height. With packing present in the fluidized bed, this dependency was much less, but packing size and shape had some effect.

Several previously proposed reactor models were considered for correlating the data.

The fluidization technique has become a widely used method of solid-gas contact over the last twenty years because of a large amount of research and development effort in both industry and universities. The quantitative design of fluidized bed reactors is, however, complicated by the bypassing of the gas via bubbles and channels, with the result that in many reactions lower conversions are obtained in a fluidized bed than in a fixed bed at the same space velocity.

Consequently, many modified reactors have been proposed to control the nature of the gas and the solid flow in the fluidized bed. For example baffles, various packings, or stirring devices have been suggested to break a deep bed into a series of shallow beds or to obtain a uniform dispersion of small gas bubbles (*1*, *2*, *3*, *4*). Overcashier et al. (*5*), Lewis et al. (*6*), and Massimilla et al. (*7*) have found that horizontal baffles improve the homogeneity of fluidized solid-gas systems, and this effect was most pronounced at high gas flow rates. Volk et al. (*8*) have used vertical surfaces such as tubes or half-rounds successfully and report that the conversion rates were the same in a 6.5-ft. diameter modified reactor as were obtained in 6-in. diameter reactor. Very little quantitative information regarding the effect of fixed packing on conversions in a fluidized bed reactor has been published. Sutherland et al. (*9*) as a result of a study of the effect of packing on fluidized bed properties such as minimum fluidization velocity, pressure drop, and heat transfer suggested that cylindrical screen packing should have useful applications in fluidized beds of free flowing materials. Gabor and Mecham (*10*) have reported data on radial gas mixing in fluidized beds containing spheres and solid cylindrical packing as part of a study on the reprocessing of spent nuclear fuels.