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Rates of Continuous Foam Fractionation of Dilute Kraft Black Liquor

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Abstract

Dilute solutions of black liquor obtained from the kraft pulping of *Pinus radiata* have been subject to continuous foam separation in laboratory-scale equipment. A power function relationship between the foam fractionation rate and both the air rate and the effluent or bottoms concentration has been established which is similar to that previously developed for binary solutions of pure surfactants.

INTRODUCTION

Foam fractionation involves the selective adsorption of a surface-active solute onto the surface of gas bubbles rising through a dilute solution and forming a foam. The foam, when collected and collapsed, forms a concentrated solution of the surface-active solute which is thus removed from the bulk of the original dilute solution. There have been several comprehensive reviews discussing the basic principles of foam fractionation (*1–3*), and the method has been widely studied for the treatment of wastewater generally although only a few researchers have investigated foaming as a process for the purification of pulp and paper mill wastes (*4–6*).

Some pulp mills already use foam separation processes as part of their operation. For example, foaming can be used as in the Lundberg black liquor oxidation process to collect sodium soap as a foam on the surface of weak kraft black liquor. The foam is separated by skimming and is then acidified to produce crude tall oil. Such a process is, however, an application of froth flotation rather than foam fractionation.

The operation of foam fractionation should be of special interest to the pulp and paper industry for at least three reasons. First, most pulp mill effluents are surface active. Their foaming tendencies are well known, and in fact the surface tension versus concentration curve of a sample of dilute pine kraft black liquor resembles that of many ordinary detergents. Second, the method operates most effectively on very dilute solutions because the slope of the surface tension versus concentration curve is greatest at low concentrations. Finally, it is difficult to imagine a potentially cheaper process for the treatment of very large quantities of effluent.

Several workers have attempted to establish the independent variables that influence a foam fractionation process so that generally applicable design procedures can be developed. These attempts have mainly been based on experiments with binary solutions of a pure surface-active material in carefully purified water, and they are not applicable to industrial effluent treatment without further investigation because they rely on the simplified form of the Gibbs adsorption equation as applied to binary solutions in pure water below the critical micelle concentration. However, one possibly useful approach for complex multicomponent effluents is that due to Grieves and co-workers (7) who developed an empirical model suitable for predicting foam fractionation rates in both batch and continuous operations.

This work showed that both the batch and continuous foam fractionation rates of a cationic surfactant, ethylhexdecyldimethylammonium bromide (EHDA-Br), could be described by a power function of the air flow rate and of the instantaneous residual surfactant concentration. (In the case of a continuous operation, the bottoms or effluent surfactant concentration was raised to the power of unity.) The accuracy of the predictive equations obtained was in the range 10 to 18%. An advantage of this simple model was that bubble size, a difficult parameter both to control and to determine, was not involved in the final equations.

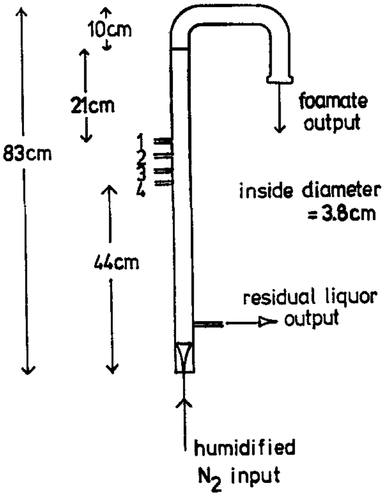
The work of Grieves and his colleagues was concerned only with a single cationic surfactant dissolved in double distilled water. However, in view of the simplicity of the approach and its obvious usefulness for work involved in the design of a pilot-scale foam fractionation plant for the treatment of pulp mill effluent, it was decided to test the applicability of the empirical model to the continuous foaming of a diluted kraft black liquor.

EXPERIMENTAL

The foam fractionation column used was a glass tube of 3.8 cm diameter and 80 cm length. A U-tube was fitted to the top of the column via a ground glass joint. Side tubes enabled different feed positions to be used. For most of the work the feed stream entered at the top position, and liquid level was maintained at a height of 21 cm above this. Nitrogen gas, saturated with water vapor in order to eliminate evaporation effects, was bubbled through a fritted glass disk in the bottom of the column. A rotameter was used to measure the nitrogen flow rate. Feed solution flowed into the column through a calibrated peristaltic pump. Flow rates of the collapsed foam and residual liquor were determined by collecting samples over a given period of time. The apparatus is illustrated in Fig. 1.

The black liquor used was a mill sample obtained from the kraft pulping of *Pinus radiata* and contained approximately 250 g of solids per liter. For the present work the concentration of this liquor and of the various streams for the foaming column was measured simply as a dry solids content by evaporation of an aliquot to constant weight.

The wavelength for maximum absorbance of the liquor was 287 nm as



(1,2,3,4 designate feed lines)

FIG. 1. Diagram of the apparatus.

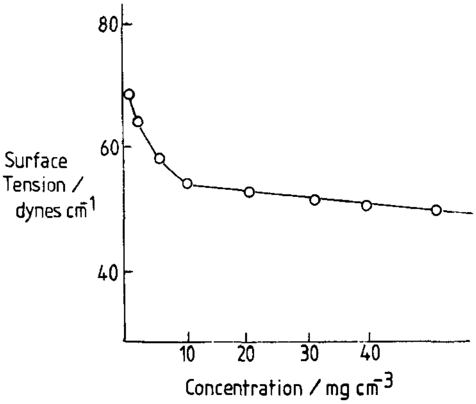


FIG. 2. Surface tension of kraft black liquor.

determined using a Shimadzu UV-200 double beam spectrophotometer with a slit width of 1 mm, recorder speed of 5 cm/min, and a deuterium light source. A linear relationship between absorbance at 287 nm and solids content was established, and so absorbance was also used as a measure of concentration for much of the work.

The surface tension of dilute solutions of the kraft black liquor was measured at 20°C using a Cambridge Du Nuoy Tensiometer (Cambridge Instrument Co., London, England), and the results are given in Fig. 2.

RESULTS AND DISCUSSION

To test the applicability of an equation of the type

$$X_fF = s(X_b)^v(G)^u \tag{1}$$

for the prediction of the continuous foam fractionation rate, X_fF, of a dilute solution of kraft black liquor, a series of continuous experiments was conducted at a single gas flow rate. The feed concentration and feed flow rate were kept constant in each experimental run, but the former was varied from run to run within the series. In each case, after steady state had been reached, the flow rate and concentrations (or absorbances) of the feed, foamate, and effluent streams were measured. Steady state was assumed to be reached when the foamate flow rate remained constant. This generally took about 2 to 3 hours.

Further series (designated Series 2 and 3) were then run using different gas flow rates. The results for three such series are given in Table 1. They are also presented in Fig. 3 where the foam fractionation rate is plotted against effluent stream concentrations on logarithmic coordinates. The three solid lines are established from a "best fit" of log (X_fF) vs log (X_b) for each series taken separately. The average percent deviations of values from the lines were 3.3% for Series 1, 4.4% for Series 2, and 3.0% for Series 3. These values compare favorably with the 11.9% average percent deviation obtained by Grieves and co-workers (*7*) for EHDA-Br solutions, especially when experimental errors, such as those involved in rotameter and pump calibrations, are considered. That these errors are significant was illustrated by comparing total mass flow rates for the feed stream with those of the two combined outflowing streams. The mean percent difference, defined by (outlet − inlet)/(inlet), was 9.2% over a total of 30 runs.

Application of the method of least squares to the results of Series 1 to 3 leads to the following values for the constants to be used in Eq. (1): $s = 1.64 \times 10^{-3}$, $u = 1.8$, and $v = 1.3$. When Eq. (1) is then used to predict foam fractionation rates, for the 30 data points given in Table 1 the average percent deviation of calculated values of X_fF from experimental values is 12.0%. For this purpose the percent deviation was defined in the same way as by Grieves et al. (*7*) who obtained a value of 18.4% for 19 data points for the foaming of EHDA-Br in a similar analysis.

The values for u and v found for the foaming of dilute kraft liquor differ markedly from the values reported by Grieves and co-workers (*7*) for the foaming of solutions of EHDA-Br. However, this is obviously produced by the use of different gas bubblers, column dimensions, foam heights, etc., and Grieves and co-workers (*7*) themselves noted that their results for the foam fractionation of EHDA-Br differed considerably from earlier work (*8*) for these reasons. It should be mentioned again that the same column, bubbler, etc. are essential in order to use the values given for predicting foam fractionation rates.

The first power on X_b found for EHDA-Br (*7*) is not validated by the present work on kraft black liquor. This is not unexpected because one would assume that this power could well depend on the surfactant used, and no work verifying the application of Eq. (1) to surfactants other than EHDA-Br has yet been reported. It is not known if the values for s, u, and v obtained in this work apply to all kraft liquors or whether they vary with the wood species being pulped and other pulping parameters. These questions may only be answered when more fundamental work determining the components of the kraft liquor responsible for surface activity is established.

TABLE 1

Cottinuous Foaming of Kraft Liquor

Run no.	F (cm^3/sec)	R (cm^3/sec)	X_f (mg/cm^3)	X_b (mg/cm^3)
Series 1 (G = 19.5 cm^3/sec; feed rate = 0.37 cm^3/sec)				
1	0.227	0.149	0.640	0.555
2	0.222	0.344	0.910	0.720
3	0.043	0.440	0.520	0.109
4	0.047	0.462	0.525	0.153
5	0.160	0.340	0.620	0.440
6	0.070	0.432	0.556	0.182
7	0.091	0.378	0.512	0.240
8	0.076	0.410	0.496	0.210
9	0.035	0.444	0.680	0.169
Series 2 (G = 24.3 cm^3/sec; feed rate = 0.37 cm^3/sec)				
11	0.059	0.434	0.492	0.103
12	0.263	0.089	0.448	0.328
13	0.124	0.289	0.360	0.170
14	0.190	0.215	0.328	0.208
15	0.201	0.257	0.372	0.222
16	0.278	0.149	0.364	0.232
17	0.279	0.096	0.476	0.380
18	0.384	0.037	0.572	0.476
19	0.270	0.149	0.388	0.280
20	0.085	0.348	0.308	0.108
21	0.294	0.148	0.400	0.284
Series 3 G = 14.0 cm^3/sec; feed rate = 0.37 cm^3/sec)				
22	0.040	0.361	0.644	0.200
23	0.051	0.337	0.588	0.246
24	0.072	0.333	0.492	0.260
25	0.073	0.328	0.656	0.304
26	0.101	0.295	0.556	0.384
27	0.107	0.276	0.648	0.464
28	0.106	0.291	0.880	0.480
29	0.136	0.262	1.070	0.830
30	0.097	0.324	0.496	0.300

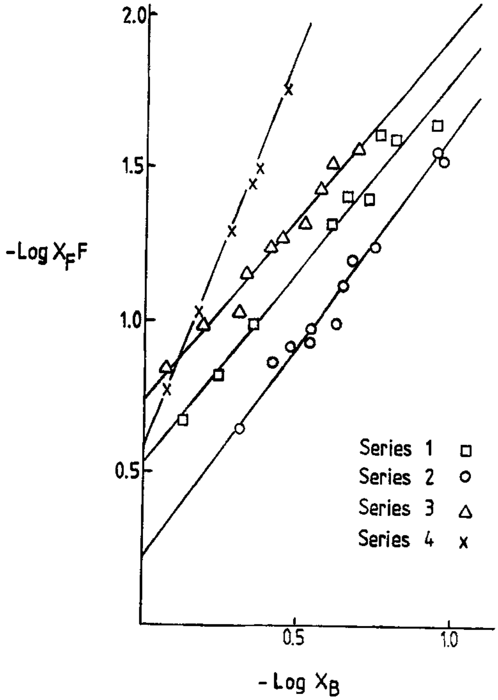


FIG. 3. Continuous foam fractionation rate vs bottoms concentration.

As outlined in the experimental section above, in this work the feed stream in all runs entered the column at a point below the liquid level. The column was thus operating in "the simple mode" (*2*) which is equivalent to one equilibrium stage plus some internal reflux due to foam collapse. It would therefore be unlikely that any major fractionation of solute components would be achieved. Some minor fractionation did occur, however, since it was noted that the relationship between solids content and absorbance at 287 nm for the original differed slightly from that for the bottoms stream. In both cases absorbance was a linear function of the solids content of the solution, as illustrated in Fig. 4. The scatter about the straight line in the case of the bottoms stream is considerable. The lower slope of this line suggests that some of the absorbing component is preferentially removed from the liquor on foaming. Considering that the kraft liquor is a complex mixture of surfactants, the results given in Fig. 4 are not surprising.

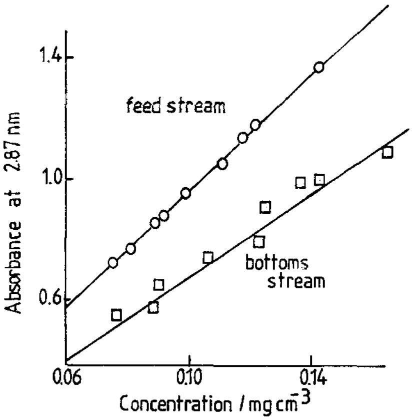


FIG. 4. Absorbance vs concentration.

With a view to increasing the separation, some different methods of foam fractionation were studied. These included (a) an increase in the height of the foam at the expense of liquid height in the column, (b) the reflux of collapsed foamate back into the ascending foam, and (c) variations in liquid pool depth without changing the height of the foam above the liquid.

The foam height was increased by introducing various feed solutions through Hole No. 4 (Fig. 1), the liquid depth being maintained at 44 cm. Nitrogen flow was set at 24.3 cm^3/sec, and overhead and bottoms collected and measured as before.

The plot of $-\log X_f F$ vs $-\log X_b$ for this series (Series 4) is also given in Fig. 3 and shows a steeper slope than that obtained for the same gas rate with a lower foam height. The greater foam height produced a higher concentration in the collapsed foamate, but the foamate flow rate was much less. This is probably explained by an increase in the collapse of foam in the column, producing internal reflux. For all runs a low foamate flow rate resulted in a high value of X_f and vice versa. Thus, as would be expected, a large foam height is desirable for obtaining a concentrated solution of surface-active solute whereas a large liquid depth is preferable to purify the solution.

The use of reflux was investigated for the dilute kraft black liquor system by feeding some of the collapsed foamate back to the top of the still foaming column by means of a peristaltic pump. However, as soon as the collapsed foamate contacted the foam in the column, the latter foam also collapsed and the column became inoperable. This effect was shown to be quite reproducible by many repetitions of the experiment. Furthermore, batchwise foam fractionation columns of the dilute kraft black liquor also ceased to foam if collapsed foamate was returned to the top of the column as reflux. A possible explanation of these observations is that foam is being formed at a concentration above the critical micelle concentration and when micelle rich foamate is recycled the micelle dissociation rate may be too low. Alternately, the surface activity of a colloidal surface-active solute may change in concentration when the foam collapses after leaving the column. Whatever the cause, this ability of refluxed foamate to collapse the foam in the column could cause difficulties if it is desired to fractionate dilute kraft spent liquors using a foaming column operating in the enriching mode.

Equation (1) can only be used for the prediction of the continuous foam fractionation rate (X_fF) if the column used is in every way identical to that for which the values of u and v were established. For example, changes in position of feed inlet, or length of foaming section, or the depth of the liquid pool may affect values of u and v. This was shown in a further series of experiments in which the depth of the liquid pool was varied as follows: Series 5, 62 cm; Series 6, 47 cm; Series 7, 25 cm. The foam height remained at 10 cm and the liquid height above the feed line was 21 cm (as in Fig. 1) but the total liquid height was varied by decreasing the overall column length to 72 cm (Series 5), 57 cm (Series 6), and 35 cm (Series 7). The results are illustrated in Fig. 5 and show that for the kraft liquor the rate of foam fractionation depends on the total height of the liquid in the column.

Grieves and co-workers (7) found that variations in liquid column height produced virtually no variation in the powers of u and v of Eq. (1) so there is a difference between the pure surfactant and the kraft black liquor in this respect. A possible reason for the difference could be the failure to achieve an ideal equilibrium stage for the kraft liquor, especially in the shorter columns. If this were so, then a higher bottoms concentration would be required for a given fractionation rate, and so the gradients of the lines of Fig. 5 would increase for shorter columns, as is found in these runs.

It should be noted that the attainment of a single equilibrium stage separation was an assumption made by Grieves and co-workers for the original model (7) on which Eq. (1) is based. However, an equation of a similar general form can be derived from mass transfer considerations even when equilibrium is not achieved, provided the column operates under

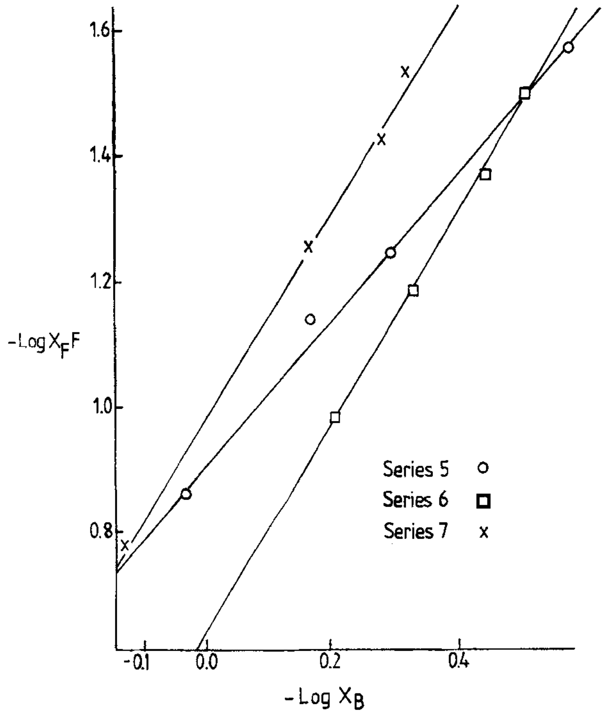


FIG. 5. Variation of liquid pool depth.

steady-state conditions. A linear relationship between $\log X_fF$ and $\log X_b$ is therefore still to be expected under nonequilibrium conditions.

CONCLUSIONS

The semiempirical Eq. (1), which has previously been applied only to an aqueous solution of the single surfactant EHDA-Br, has been shown to apply equally well to a highly complex multicomponent surfactant mixture, namely dilute kraft black liquor. The foam fractionation rate for the continuous foaming of this liquor could be predicted from

$$X_fF = 1.64 \times 10^{-3}G^{1.8}X_b^{1.3}$$

provided that the foaming was conducted in the same column but at variable feed concentrations, feed rates, and gas flow rates. The accuracy of the equation is about 12%, although for foaming at a single gas flow rate a simplified equation of the form

$$X_f F = k X_b^{1.3} \tag{2}$$

gives an accuracy of about 4%.

SYMBOLS

F	flow rate of foam stream (collapsed, as liquid), cm^3/min
G	gas flow rate, cm^3/min
k	constant in Eq. (2)
X_b	kraft liquor concentration in bottoms or effluent stream, mg/cm^3
X_f	kraft liquor concentration in foam stream, mg/cm^3
s, u, v	coefficients or powers in Eq. (1)
R	flow rate of bottoms stream, cm^3/min

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