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THE FOAM SEPARATION OF SOME POLYSACCHARIDE MIXTURES

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ABSTRACT

The method of foam fractionation has been applied to four different polysaccharide mixtures, and in each case, partial fractionation occurred. Both batch and continuous foaming were used, and for the latter, the results of working with polysaccharide–surfactant mixtures are described. The actual fractionations achieved are not large, but, because of its simplicity, the method is valuable for assessing the homogeneity of some polysaccharides. In several of the continuous runs, the rate of foam fractionation is shown to be a power function of the concentration of residual polysaccharide.

INTRODUCTION

Foam fractionation is a separation technique that is based on the selective adsorption of surface-active molecules at the surface of bubbles which rise through a column of liquid and produce a foam[1]. It has been studied as a means of removing surface-active solutes from solution, and for the fractionation of surface-active compounds. For a single, nonionic, surface-active solute in a dilute solution, the concentration of solute at the surface can be expressed by

$$\Gamma = -\frac{1}{RT} \cdot \frac{d\gamma}{d\ ln\ a}, \qquad (1)$$

where Γ is the surface excess of surfactant, γ is the surface tension, and a is the activity of the surfactant. In dilute solutions in which the activity coefficient may be taken as equal to unity, Eq. *1* may be written

$$\Gamma = -\frac{c}{RT} \cdot \frac{d\gamma}{dc}, \qquad (2)$$

where c is the concentration of the surfactant. The quantity $d\gamma/dc$ is the gradient of the plot of surface tension *versus* concentration for a two-component system. If a solute causes a decrease in surface tension, $d\gamma/dc$ is negative, and Eq. *2* shows that there is adsorption on the surface.

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The first work on the foam fractionation of polysaccharides was performed by Schütz[2], who foamed solutions of *O*-methylcellulose, and found that some fractionation occurred on the basis of molecular size and methoxyl content. It is surprising that no further foam-fractionation studies of polysaccharides have been reported since Schütz's early work.

To assess the general applicability of the method, four different polysaccharides were selected for study, namely, (I) a water-soluble polysaccharide prepared from the wood meal of *Pinus radiata*[3], (II) a water-soluble holocellulose fraction from the same wood, (III) a xylan prepared from the dried leaves of the snow tussock *Chionochloa rigida*, and (IV) a commercial *O*-methylcellulose preparation. These polysaccharides were chosen on the basis of their ready availability plus the fact that their solutions all exhibit some degree of surface activity and frequently show foaming tendencies during isolation.

RESULTS AND DISCUSSION

Preliminary experiments were undertaken to measure the effect of the concentration of the polysaccharide solution on the surface tension, and the results are given in Figs. 1 to 4. The curves, similar to those given by synthetic surfactants, show the concentration range over which the gradient $d\gamma/dc$ is a maximum, and it is in this range of concentration, if Eq. *1* or *2* is applicable, that the highest rate of foam fractionation of the surface-active solute should occur. The concentrations of polysaccharide solutions used for the foam-fractionation experiments were chosen on this basis.

Three separate, batch, foam-fractionation experiments were therefore conducted on the water-soluble polysaccharide, using liquor concentrations of 1.3, 2.6, and 4.0 g.L^{-1}. In each experiment, three foamate fractions were collected as de-

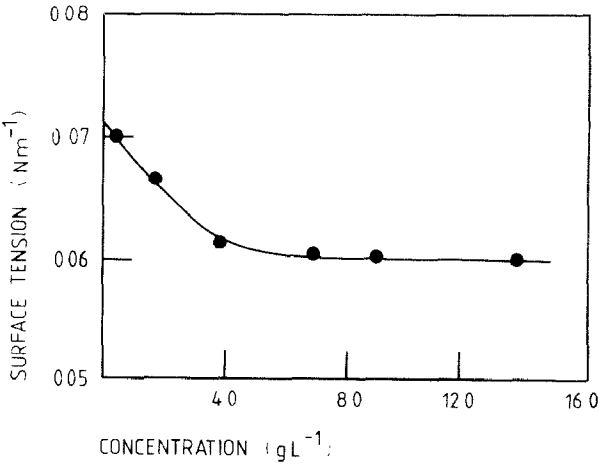

Fig. 1 Surface tension of water-soluble polysaccharide from *Pinus radiata*

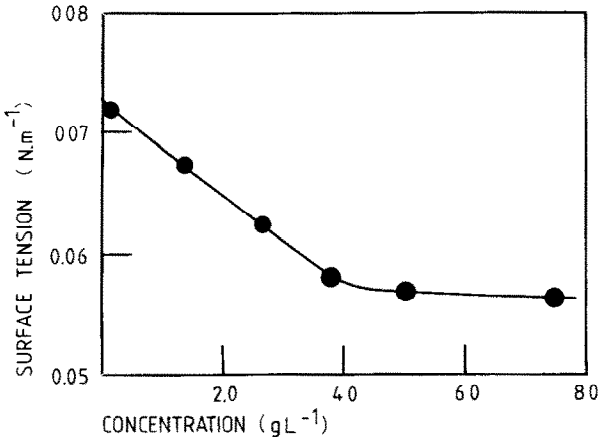

Fig. 2. Surface tension of a water-soluble holocellulose from *Pinus radiata*.

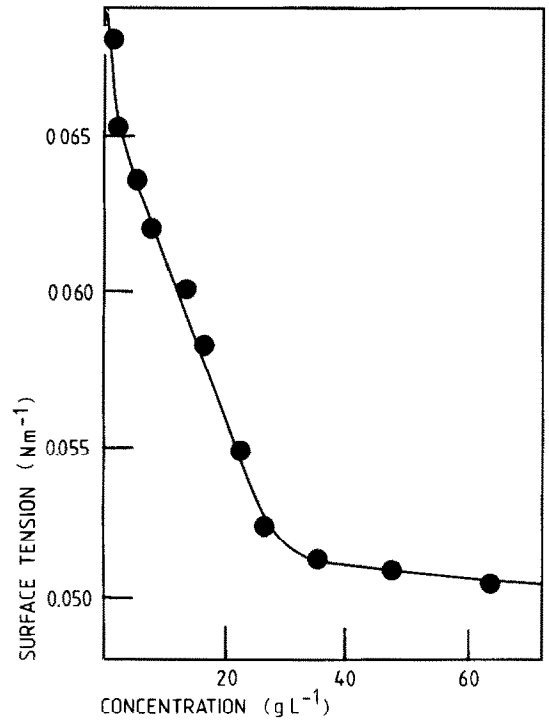

Fig. 3. Surface tension of a xylan from the snow tussock *Chionochloa rigida*.

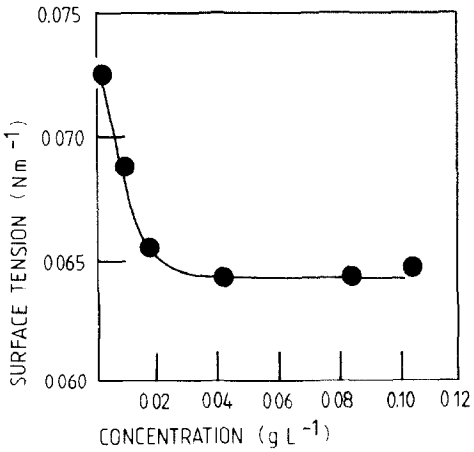

Fig. 4. Surface tension of a commercial *O*-methylcellulose.

scribed in the Experimental section. If any enrichment of one component of the water-soluble polysaccharide occurred during foaming, it should be most marked in the first foamate fraction collected, and this is, in fact, the case. The data reported in Table I show that, in all experiments, the hydrolyzate of the first fraction contained the highest ratios of arabinose:mannose, galactose:glucose, arabinose:glucose, and arabinose:xylose.

Previous structural work on the water-soluble, polysaccharide fraction from *Pinus radiata* showed that it contains at least two different polysaccharides[3]. The first of these is a highly branched arabinogalactan in which the ratio of L-arabinose to D-galactose residues is ~1:8. Detailed, structural work on the second polysaccharide has not yet been reported, but it is known that its analysis agrees with that calculated for a galactoglucomannan in which the ratios of mannose:galactose:glucose residues are 3.4:1.5:1.0.

The results obtained from the batch foaming of the water-soluble polysaccharide show that the arabinogalactan polysaccharide is preferentially removed from solution by foaming. This is illustrated most clearly by the values obtained from the arabinose:mannose ratios and the arabinose:glucose ratios in the various fractions reported in Table I. The arabinogalactan contains no mannose or glucose, and the galactoglucomannan contains no arabinose. Thus, the ratio of either arabinose:mannose or arabinose:glucose in any fraction will be a measure of the relative amounts of arabinogalactan to galactoglucomannan in the fractions. The three experiments detailed in Table I show that, in all of them, the first foamate fraction collected is richer in arabinogalactan than the solution left at the completion of the batch experiment. Furthermore, as would be expected, the ratio of arabinogalactan to galactoglucomannan is, in all instances, less in the residual than in the original solution, but the ratio of arabinose:galactose remains constant in all

TABLE I

BATCH FOAM-FRACTIONATION OF A WATER-SOLUBLE POLYSACCHARIDE FROM *Pinus radiata*

Fraction	*1*	*2*	*3*	*Residue*	*Original*	*1*	*2*	*3*	*Residue*	*Original*	*1*	*2*	*3*	*Residue*	*Original*
Arabinose/xylose	9.7	9.6	9.1	9.4	9.4	10.4	8.8	8.9	9.1	9.4	9.9	8.3	8.7	8.5	9.5
Arabinose/glucose	1.4	1.2	1.3	1.2	1.6	1.7	1.5	1.3	1.5	1.6	1.7	1.4	1.4	1.5	1.6
Xylose/mannose	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Galactose/glucose	18.6	15.8	15.4	12.4	15.4	17.7	16.3	15.9	14.3	15.5	16.5	16.4	15.0	13.5	15.3
Arabinose/galactose	0.10	0.10	0.11	0.10	0.10	0.11	0.11	0.10	0.11	0.10	0.12	0.10	0.11	0.11	0.11
Xylose/glucose	0.16	0.16	0.16	0.17	0.17	0.17	0.17	0.15	0.17	0.17	0.17	0.17	0.16	0.16	0.17
Arabinose/mannose	3.8	3.7	3.5	2.7	3.4	3.6	3.3	3.5	2.9	3.3	3.7	3.4	3.5	2.9	3.1
Gas flow-rate ($mL.min^{-1}$)	635–960					475–855					630–960				
Solute concentration ($g.L^{-1}$)	1.3					2.7					4.0				

TABLE II

BATCH FOAM-FRACTIONATION OF A WATER-SOLUBLE HOLOCELLULOSE FROM *Pinus radiata*

Fraction	*1*	*2*	*3*	*Residue*	*Original*	*1*	*2*	*3*	*Residue*	*Original*	*1*	*2*	*3*	*Residue*	*Original*
Arabinose/xylose	0.28	0.33	0.34	0.50	0.40	0.33	0.35	0.34	0.44	0.40	0.32	0.42	0.41	0.38	0.39
Arabinose/mannose	0.04	0.05	0.06	0.07	0.06	0.05	0.05	0.05	0.06	0.06	0.05	0.06	0.06	0.07	0.06
Arabinose/glucose	0.12	0.16	0.18	0.24	0.21	0.16	0.18	0.18	0.23	0.21	0.15	0.20	0.20	0.27	0.21
Xylose/glucose	0.46	0.49	0.51	0.55	0.53	0.48	0.46	0.52	0.53	0.53	0.45	0.46	0.48	0.57	0.51
Xylose/mannose	0.14	0.14	0.17	0.15	0.15	0.14	0.14	0.16	0.16	0.15	0.15	0.15	0.16	0.15	0.16
Galactose/glucose	1.13	1.38	1.41	1.89	1.60	1.32	1.45	1.41	1.65	1.55	1.27	1.37	1.41	1.55	1.49
Arabinose/galactose	0.11	0.11	0.12	0.10	0.12	0.11	0.12	0.12	0.12	0.13	0.11	0.13	0.13	0.13	0.13
Gas flow-rate ($mL.min^{-1}$)	745					225					210				
Solute concentration ($g.L^{-1}$)	1.3					2.7					4.0				

fractions, indicating that these two monosaccharides form part of the same polysaccharide.

It should be pointed out that there are several anomalies in the results reported in Table I. These probably arise from errors associated with the gas–liquid chromatographic analysis. However, the standard deviations for the various monosaccharide ratios were shown to be arabinose:mannose = 2.0, galactose:glucose = 1.9, arabinose:glucose = 3.4, xylose:glucose = 2.6, and xylose:mannose = 3.8%. Thus, the general conclusion just reached concerning the partial fractionation of the water-soluble polysaccharide is valid.

The original, water-soluble polysaccharide also contained some xylosyl residues. The results in Table I suggest that the xylose-containing component is probably associated more with galactoglucomannan than with arabinogalactan, and is not selectively removed from solution by foaming. However, the low content of xylose makes determination of small differences in the xylose ratios unreliable.

Three separate experiments on the batch foam-fractionation of the water-soluble holocellulose were also conducted, using the same feed concentrations as for the previous experiments. Three foamate fractions from each experiment were collected. The data given in Table II show that, in all experiments, the first foamate fraction contained the lowest ratios of arabinose:xylose, galactose:glucose, arabinose:mannose, and arabinose:glucose.

The study of the batch foam-fractionation of the water-soluble holocellulose from *Pinus radiata* was undertaken as a preliminary to a detailed, structural analysis of the polysaccharide mixture. Thus, no structural analysis was available when the foam-fractionation work was performed. However, the holocellulose probably represents cell-wall polysaccharide of very low molecular weight which was degraded during the delignification process, combined with some of the typical, softwood water-soluble polysaccharides (such as the arabinogalactan) which were not initially soluble in water, but became so after the removal of lignin. It would thus be expected that the water-soluble holocellulose should contain a mixture of low-molecular-weight galactoglucomannan, acidic arabinoxylan, and arabinogalactan fractions.

The results described in Table II show that the arabinogalactan type of polysaccharide is less readily removed from solution by foaming than the polysaccharides that contain mainly xylosyl, or glucosyl and mannosyl residues. The low arabinose:xylose, arabinose:mannose, and arabinose:glucose ratios support this conclusion, and the fact that the xylose:glucose and xylose:mannose ratios remain more or less constant for all of the fractions indicates that either these monosaccharides are constituents of a single polysaccharide or, alternatively, the polysaccharides which contain them are removed to a similar extent on foaming.

Three solutions of the xylan isolated from the leaves of *Chionochloa rigida*, of concentrations 1.3, 2.6, and 4.0 $g.L^{-1}$, were subjected to separate, batch foam-fractionation, and three foamate fractions were collected. The data reported in Table III show that, in all of these experiments, the first foamate fraction contained

TABLE III

BATCH FOAM-FRACTIONATION OF A XYLAN FROM SNOW GRASS *(Chionochloa rigida)*

Fraction	*1*	*2*	*3*	*Residue*	*Original*	*1*	*2*	*3*	*Residue*	*Original*	*1*	*2*	*3*	*Residue*	*Original*
Xylose:arabinose ratio	2.8	3.0	2.9	3.0	3.1	2.8	2.9	2.8	3.2	3.1	2.8	2 8	2.9	3.3	3.1
Gas flow-rate ($mL.min^{-1}$)	430					325					215				
Solute concentration ($g.L^{-1}$)	1.3					2.6					4.0				

the lowest ratio of xylose:arabinose, and the ratio of xylose:arabinose is higher in the residual solution in two experiments.

The original, xylan fraction of snow tussock also contained traces of galactose and glucose. However, because of the low content of total hexose, these two components of the polysaccharide hydrolyzate were not studied further.

The partial foam-fractionation of the snow-tussock xylan shows that this polysaccharide is not homogeneous, but should be regarded as a mixture of at least two different arabinoxylans in which the xylose:arabinose ratios differ. Most of the reported structural investigations of plant xylans usually imply homogeneity, although some work[4] shows that there are instances where there is more than one arabinoxylan present.

In addition to studying the changes in individual polysaccharide content of liquors which are foamed, it is also desirable to study the rate of removal of material during foaming, as rate data will always be necessary if any large-scale separation-process is to be developed. It is possible to obtain rate data from even the simple type of batch foam-fractionation process used in this work, and such an analysis was reported by Grieves *et al.*[5], who showed that, at any instant in a batch-foaming operation, the separation rate is given by

$$\frac{-\mathrm{d}(C_b V_b)}{\mathrm{d}t} = S(V_g)^W (C_b)^V, \tag{3}$$

where t = time, C_b = concentration and V_b= volume of raffinate in batch foaming, V_g = volumetric gas flow-rate, and S, W, and V were assumed to be constant for any particular system. This model, as developed by Grieves *et al.*, applied only to pure solutions of a single, cationic surfactant. Attempts were made to test this model for the polysaccharide solutions under study, using the same method of interpreting batch-foaming data as used by Grieves *et al.* The results in our case were inconclusive, mainly because the foam-fractionation rates achieved were too low for precise measurements to be made.

There are many limitations to batch-foaming operations, including theoretical difficulties in analyzing results (because the operation is non-steady-state) and practical difficulties of reproducibility. However, preliminary experiments on the continuous foaming of the water-soluble polysaccharide, the water-soluble holocellulose, and the xylan showed that these three polysaccharides were extremely difficult to foam continuously, unless additional surfactants were added. This was because the foam produced was so unstable that high concentrations of polysaccharide were necessary, and, furthermore, continuous foam-fractionation often took several hours after starting to settle down to a steady state. Thus, invariably, large quantities of polysaccharide solution were required for each continuous run. A decision was, therefore, made to study the continuous foam-fractionation of three polysaccharides in the presence of added surfactants, and only in the case of

O-methylcellulose was any attempt made to foam a polysaccharide continuously in the absence of added surfactant.

The addition of surfactants in order to assist the foam fractionation of a wide variety of materials has been extensively investigated over the last decade, and both organic and inorganic solutes have been removed from aqueous solution in this way. For example, Grieves and Aronica [6] investigated the foam separation of phenol by addition of ethylhexadecyldimethylammonium bromide (EHDA-Br). Their limited success was improved on by Ervin and Danner[7], who used continuous foam-fractionation with reflux. The removal of inorganic species is illustrated by the work of Phillips *et al.*[8], who used a cationic surfactant for the foam separation of phosphate.

For the present work, two surfactants were selected for addition to the polysaccharide before continuous foaming. The first of these was Triton X-100 [isooctylphenoxypoly(ethoxyethanol)], which was chosen mainly because of the large amount of published work involving the foaming of this surfactant. For example, Jashnani and Lemlich[9] used Triton X-100 in their application of the transfer-unit concept to foam fractionation, and Aguayo and Lemlich[10] used the same surfactant when assessing counter-current foam-fractionation at high rates of throughput by means of perforated-plate columns.

It would be expected that Triton X-100, being nonionic, would not form any strong chemical complex with polysaccharides, especially neutral polysaccharides. However the second surfactant selected for addition to the polysaccharides before foaming was cetyltrimethylammonium bromide (CTAB), which is a cationic surfactant and was selected mainly because of its known complex-formation with some polysaccharides[11–13]. The best known examples are those in which the polysaccharide contains uronic acid groups, in which case, the complex is usually insoluble under the conditions used. However, the work of Fishman and Miller[14] shows that complex-formation also occurs between CTAB and polysaccharides that do not contain acidic groups. CTAB has previously been used in foam-fractionation studies. For example, Grieves and Bhattacharyya[15,16] investigated the effect of the reagent on the separation of a solution of stannic oxide by foaming.

One of the important reasons for studying continuous foam-fractionation of polysaccharide solutions is that fractionation-rate data can be obtained which would be valuable should the operation prove to have any commercial application. The rate of continuous foam-fractionation was originally correlated with experimental parameters by Grieves *et al.*[5], who developed an empirical model relating the rate of foam fractionation in a continuous process to the gas rate and the raffinate concentration, and thus showed that

$$C_f V_f = S(V_g)^W (C_r)^V, \tag{4}$$

where S, W, and V are assumed to be constant for any particular system, C_f = con-

centration of collapsed foamate stream, V_f = volumetric flow-rate of collapsed foamate stream, and C_r = concentration of raffinate in continuous foaming.

This equation was applied to the continuous foaming of an aqueous solution of *O*-methylcellulose. A series of continuous experiments was conducted at a single, gas-flow rate. The feed concentration and feed flow-rate were kept constant during each run, but were varied from run to run within the series. In each case, after steady state had been reached, the flow rates and concentrations of the feed, foamate, and raffinate streams were measured. Steady state was considered to be reached when the foamate and raffinate flow-rates remained constant. A plot of log C_fV_f *versus* log C_r was fitted by regression analysis to a straight line described by the equation $\log C_fV_f = 1.16 \log C_r - 0.61$, as shown in Fig. 5. The correlation coefficient of the individual data-points in relation to the fitted line is 0.97. The average, percent deviation, as defined by Grieves *et al.*[5], is ~20%, which compares favorably with the results of Grieves *et al.*, in view of the wider range of fractionation rates covered in this work.

It can be shown[17] that, in continuous, countercurrent foam-fractionation using a single column operating under steady-state conditions, the concentration, C_o, of surface-active solute in the feed solution is related to the concentration, C_r, in the raffinate by the equation

$$\frac{C_o}{C_r} = 1 + \frac{V_g A \Gamma_r}{V_o C_r}, \tag{5}$$

where A = surface area of foam bubble per unit volume, Γ_r = surface excess of polysaccharide in equilibrium with raffinate solution, in continuous foaming, and

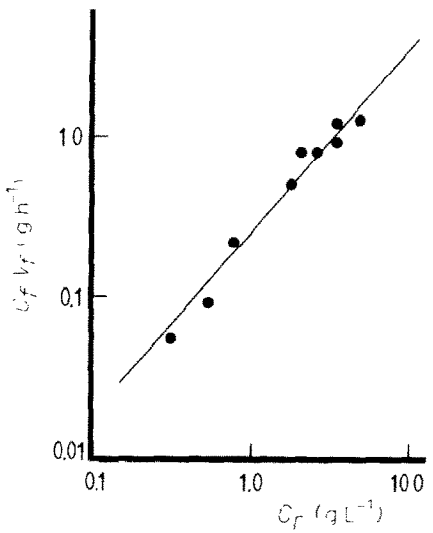

Fig 5. Rates of continuous foaming of *O*-methylcellulose solutions

TABLE IV

CONTINUOUS FOAMING OF *O*-METHYLCELLULOSE

V_g ($mL.min^{-1}$)	V_o ($mL.min^{-1}$)	V_f ($mL.min^{-1}$)	V_r[a] ($mL.min^{-1}$)	A (cm^{-1})	C_o ($g.L^{-1}$)	C_r ($g.L^{-1}$)	C_f ($g.L^{-1}$)	C_o/C_r	Γ_r ($g.m^{-2}$)
69.0	3.3	1.9	1.3	20.0	0.35	0.31	0.47	1.13	0.96×10^{-3}
74.0	5.7	2.2	3.5	26.5	0.63	0.54	0.67	1.17	2.7×10^{-3}
74.0	11.3	4.9	6.6	26.9	0.80	0.73	0.83	1.10	4.1×10^{-3}
74.0	6.1	3.6	2.5	26.0	1.75	1.61	1.97	1.09	4.6×10^{-3}
74.0	9.7	6.0	3.7	23.1	2.17	2.07	2.23	1.05	5.9×10^{-3}
74.0	7.1	4.8	2.3	24.3	2.68	2.49	2.89	1.08	7.8×10^{-3}
54.0	6.8	5.0	1.8	25.3	3.45	3.26	3.72	1.06	9.7×10^{-3}
45.0	6.2	3.4	2.8	22.1	3.91	3.74	4.37	1.05	1.1×10^{-2}
30.0	6.1	3.8	2.3	22.1	5.14	5.02	5.25	1.02	1.1×10^{-2}

[a] V_r = volumetric flow-rate of raffinate stream in continuous foaming.

V_o = volumetric flow-rate of feed stream in continuous foaming. Eq. 5 was used in order to determine the equilibrium relationship between Γ_r and C_r for *O*-methylcellulose solutions from the experimental results obtained from the continuous, foam-fractionation rate-studies in the experiments just described. The results are presented in Table IV and Fig. 6.

From the figure, Γ_r is seen to be nearly proportional to C_r over the low-concentration range, *i.e.*, the distribution coefficient Γ_r/C_r is approximately constant. At high concentrations, the curve becomes horizontal. The slope is, in general, similar to that obtained by other methods used for determining the surface excess of surfactants, and can be readily explained by the usual theories of surface chemistry. One use of such equilibrium curves stems from the fact that they are required for the design of multistage, foam-fractionation columns for the removal of a given species[18].

We have also used Eq. 5 to study the variation of the distribution coefficient, Γ_r/C_r, for *O*-methylcellulose at a concentration of 1.65 g.L^{-1} in solutions of Triton X-100 of differing concentrations. The results are summarized in Table V and Fig. 7, and show that the distribution coefficient is a maximum when no Triton X-100 is used; and furthermore, after the substantial decrease following the initial addition of Triton X-100, the coefficient continues to decrease steadily with increasing concentration of Triton X-100. If Triton X-100 and *O*-methylcellulose formed a surface-active complex, a maximum would be expected in Fig. 7. The results therefore imply that no complex is formed, and that Triton X-100 and *O*-methylcellulose compete for adsorption at the foam-bubble surface.

The previous determinations of surface excess depend on the estimation of A, the interfacial area per unit volume of air in the foam. This was calculated by using the equation

$$A = 6\frac{\Sigma n_i d_i^2}{\Sigma n_i d_i^3},$$

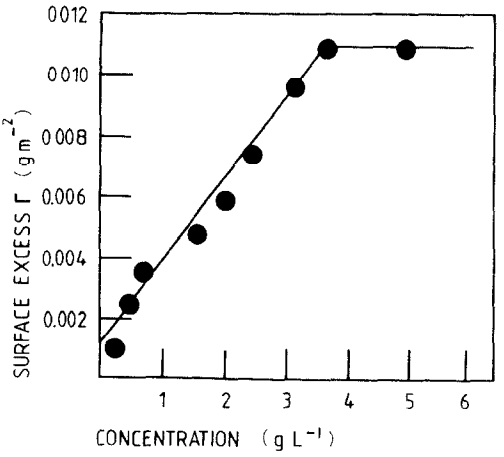

Fig. 6. Surface excess measurements of *O*-methylcellulose solutions.

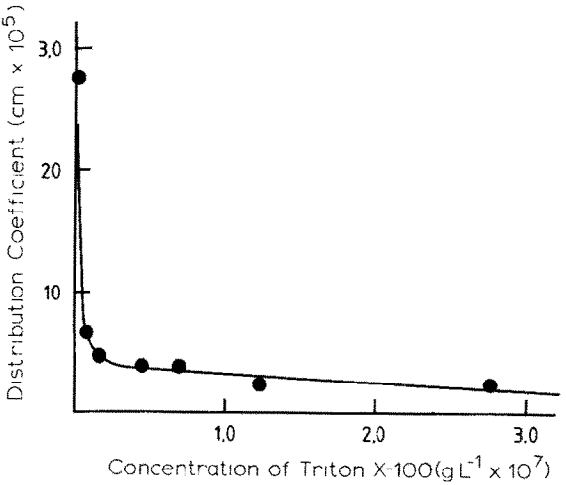

Fig. 7. Effect of concentration of Triton X-100 on adsorption of *O*-methylcellulose.

where d_i = diameter of a foam bubble, and n_i = number of foam bubbles of diameter d_i. The use of the factor 6 is considered appropriate for our prediction of A, as most of the bubbles observed were spherical. The value of A calculated for a given species over the concentration ranges used in this study is approximately constant, provided that the foams have a low density and very little drainage of foam occurs.

Results from the continuous foaming of Triton X-100–water-soluble polysaccharide are given in Table VI, in which the results for three runs are presented. In runs 1 and 2, the concentration of polysaccharide in the feed solution was 0.81 $g.L^{-1}$, and that of Triton X-100 was 0.8 $g.L^{-1}$; in run 3, these were lowered to 0.56 and 0.58 $g.L^{-1}$, respectively. Run 1 differed from run 2 in that, in the latter, the feed went into the foamate. The rate of gas flow was, in all cases, 54 $cm^3.min^{-1}$, and the feed rate was 1.66 $cm^3.min^{-1}$. The hydrolyzates of the feed, raffinate, and foamate streams were analyzed for monosaccharides, and the various monosaccharide ratios were determined. In all runs, the foamate fractions contained the largest galactose:glucose, arabinose:glucose, and arabinose:xylose ratios. This suggests that an arabinose- and galactose-containing polysaccharide was selectively removed to a larger extent than glucose- and mannose-containing polysaccharide. Furthermore, the xylose:mannose and xylose:glucose ratios also show that no fractionation of xylose-containing polysaccharides with respect to glucomannan had occurred. It is noteworthy that the arabinose:galactose ratios do not change in either the foamates or raffinates of the three experiments. This shows that, within the galactose- and arabinose-containing polysaccharide, no obvious partial-fractionation could be detected. The standard deviations are considered to be the same as that of batch foaming of the water-soluble polysaccharide. Overall, the results show that the polysaccharide fractionation achieved in the continuous experiments is no better than that obtained in the batch foaming, described earlier, of the water-

TABLE V

THE VARIATION OF DISTRIBUTION COEFFICIENT OF *O*-METHYLCELLULOSE WITH CONCENTRATION OF TRITON X-100

V_g (*mL min*$^{-1}$)	V_o (*mL min*$^{-1}$)	V_1 (*mL min*$^{-1}$)	V_f (*mL.min*$^{-1}$)	A (cm^{-1})	C_o ($g.L^{-1}$)	C_f ($g\ L^{-1}$)	C_1 ($g\ L^{-1}$)	C_o/C_f	C_r (*Triton*) ($g.L^{-1}$)	Γ/C_r (*cm*)
54.0	4.1	3.2	0.8	31.4	1.72	1.67	1.75	1.03	0.9×10^{-8}	7.2×10^{-5}
54.0	4.1	2.1	2.0	32.8	1.64	1.61	1.67	1.02	1.8×10^{-8}	4.3×10^{-5}
54.0	4.1	2.1	2.0	33.4	1.68	1.66	1.71	1.01	4.4×10^{-8}	2.7×10^{-5}
54.0	4.1	2.1	2.1	34.2	1.64	1.61	1.68	1.02	7.2×10^{-8}	4.1×10^{-5}
54.0	4.1	2.3	1.8	31.2	1.60	1.58	1.63	1.01	1.2×10^{-7}	3.1×10^{-5}
54.0	4.0	2.3	1.7	31.3	1.71	1.69	1.72	1.01	2.8×10^{-7}	2.8×10^{-5}

TABLE VI

CONTINUOUS FOAMING OF TRITON X-100 + WATER-SOLUBLE POLYSACCHARIDE

	Run 1			*Run 2 (Feed on foamate)*			*Run 3*		
	Feed	*Raffinate*	*Foamate*	*Feed*	*Raffinate*	*Foamate*	*Feed*	*Raffinate*	*Foamate*
Arabinose/xylose	9.5	9.2	9.8	9.4	9.1	10.0	9.6	9.3	10.1
Arabinose/glucose	1.5	1.2	1.9	1.7	1.3	1.9	1.6	1.4	1.9
Xylose/mannose	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.3	0.4
Galactose/glucose	15.7	13.1	17.1	14.9	12.8	18.7	15.6	11.3	18.8
Arabinose/galactose	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Xylose/glucose	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2

soluble polysaccharide. Thus, the use of Triton X-100 would not appear to assist in any way in the foam fractionation of the water-soluble polysaccharide. It is likely that no complex between Triton X-100 and this polysaccharide is formed.

Feed on foamate in the second experimental run did not appear to have any major effect on the fractionation. However, it does give a little better polysaccharide and surfactant removal from solution.

The results of a series of continuous, foam-fractionation runs on mixtures of water-soluble polysaccharide and CTAB are summarized in Fig. 8, which relates the raffinate concentration of each individual polysaccharide component to the foam-fractionation rate of that polysaccharide. The ranges of concentration covered are limited by the composition of the original, water-soluble polysaccharide. The concentrations of the component polysaccharides in each stream of the continuous-foam-fractionation apparatus were determined by g.l.c. analysis of the acid hydrolyzate of each stream, coupled with the known monosaccharide composition of the separated polysaccharides[3]. The solid line A of Fig. 8 was established by linear-regression analysis of log C_fV_f *versus* log C_r for the water-soluble galactoglucomannan. The equation of line A is log $C_fV_f = 0.54 \log C_r - 1.30$, and the correlation coefficient of the individual data-points in relation to the fitted line is 0.95. The solid line B of Fig. 8 refers to the results obtained for the arabinogalactan; its equation is log $C_fV_f = 0.48 \log C_r - 1.03$, and the correlation coefficient is 0.90. These correlation coefficients result from the analytical methods used, and are not a reflection of inapplicability of Eq. *4* to the polysaccharide system under study.

The results obtained from the continuous foaming of the water-soluble polysaccharide thus show a foam-fractionation rate that is consistent with a power-law equation, such as Eq. *4*. However, as the equations of the "best fit" lines show, the behavior of the two polysaccharides, *i.e.*, the arabinogalactan and the galactoglucomannan, is very similar, and this is probably because both polysaccharides form separate complexes with CTAB, and the surface properties of the complex are dominated by that of CTAB itself. Thus, the complexes themselves have similar, surface properties and compete almost equally for adsorption sites at the sur-

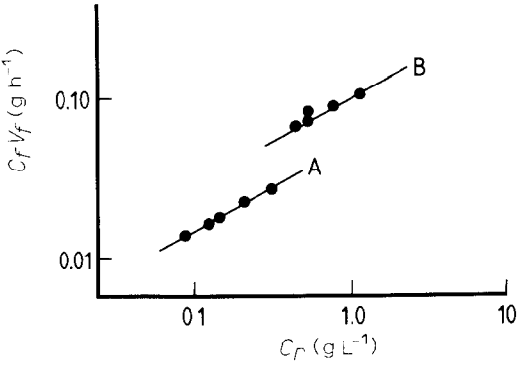

Fig. 8. Continuous foaming of water-soluble polysaccharides from *Pinus radiata*.

face of a foam bubble. It therefore follows that continuous foaming of the CTAB–water-soluble polysaccharide system provides a good procedure for removing the polysaccharide from dilute aqueous solution, but it does not serve as a method for fractionating the polysaccharide into its two major components. This conclusion was supported by the results of many g.l.c. analyses of the three streams (feed, foamate, and raffinate) of a continuously foaming column of CTAB–water-soluble polysaccharide solution, when no fractionation was achieved over a very wide range of operating conditions.

TABLE VII

CONTINUOUS FOAM FRACTIONATION OF XYLAN–CTAB MIXTURES

Run number	*1*	*2*	*3*
Xylan concentration in feed (g L^{-1})	1.45	1.91	2.81
CTAB concentration in feed (g L^{-1})	0.075	0.075	0.075
Feed flow-rate (cm^3 min^{-1})	1.66	1.66	1.66
Gas flow-rate (cm^3 min^{-1})	54	54	54
Xylan concentration in raffinate (g L^{-1})	1.25	1.68	2.51
Xylan concentration in foamate (g L^{-1})	2.52	2.76	4.00
Xylose/arabinose ratio in feed	3.1	3.1	3.1
Xylose/arabinose ratio in raffinate	3.5	3.4	3.4
Xylose/arabinose ratio in foamate	2.8	2.7	2.9
Temperature (degrees)	20	20	20

The final system studied involved the continuous foaming of CTAB–xylan solution. The results, presented in Table VII, show that arabinose-rich xylan is selectively removed from solution by continuous foaming, which supports the results obtained from batch, foaming experiments. In three experiments presented in Table VII, the hydrolyzates of all of the foamate fractions have a lower content of xylose than those of the raffinate fractions. Furthermore, the raffinate fractions collected contained a higher content of xylose than the feed solutions. The results of the monosaccharide ratios obtained from the continuous foaming of the xylan with CTAB are more marked compared with the batch foaming of the xylan. It would thus appear that the use of CTAB does assist in the partial fractionation of the xylan by continuous foaming.

From these results, it is concluded that some polysaccharides are readily removed from dilute, aqueous solution by foam fractionation, either with or without addition of a surfactant capable of forming a surface-active complex with the polysaccharides. Measurement of the rate of removal by foaming shows that this can be related by a power-function equation to both the gas flow-rate and the bottoms concentration, as has been shown for the foaming of a binary solution of a pure surfactant[5]. The actual fractionation achieved in this study is not large, but as the experimental conditions used in all of the foaming experiments described were

equivalent to only a single equilibrium-stage, it may be assumed that fractionations would be greatly improved by multistage operation.

EXPERIMENTAL

Materials. — The water-soluble polysaccharide of *Pinus radiata* was isolated from fresh sapwood obtained from the City Corporation Forests, Dunedin, New Zealand. Extractive-free wood-meal was prepared by Soxhlet extraction of ground wood with 2:1 (v/v) benzene–ethanol, and the dried meal was then extracted three times with water. The water-soluble polysaccharide was obtained in 1% yield from the combined extracts by precipitation by pouring into ethanol.

The wood residue from this extraction was converted into holocellulose by the method of Wise and Jahn[19]. The holocellulose was then extracted with water at 20°, and the water-soluble holocellulose isolated by precipitation by pouring into ethanol. The yield was 2% (on an oven-dried-wood basis).

The xylan sample was isolated from snow tussock grass (*Chionochloa rigida*) growing in Central Otago, New Zealand. Extractive-free leaves were delignified by the holocellulose method[19], and the xylan was separated from the grass holocellulose by the barium-impregnation procedure developed by Hamilton and coworkers[20].

The *O*-methylcellulose sample used was laboratory grade (400 cP; 400 mPa.s), supplied by the Chemical Manufacturing Division of Fisher Scientific Company, U.S.A.

General methods. — The surface tensions of polysaccharide solutions were determined at 20° by the drop-weight method[21], the surface tensions being calculated from the tables of Harkins and Brown[22]. Concentrations of CTAB in aqueous solutions were measured by the sodium tetraphenylboron solution method, which was developed by Cross[23] for cationic-surfactant solutions, and concentrations of Triton X-100 in aqueous solutions were measured by comparing the absorbance of the solutions at 273.8 nm with the absorbance obtained for standard solutions of Triton X-100. The total concentration of polysaccharide in solution was analyzed colorimetrically by the phenol–sulfuric acid method of Dubois *et al.*[24]. The method was checked with standard solutions of the four polysaccharides studied.

Batch-foaming method. — The apparatus used is illustrated in Fig. 9. Nitrogen gas was led through a rotameter type of flow meter to a humidifier, and thence through a porous-glass sparger into the glass, foam-fractionation column (28 × 2.5 cm i.d.). The column was clamped in a vertical position, and into its top was fitted a U-tube of similar diameter. The solution to be foamed (150 mL) was placed in the column, the U-tube positioned, and the nitrogen flow adjusted to a predetermined value. Three collapsed, foamate fractions were collected, and these fractions, the residual liquid, and the original solution were sampled for analysis.

For the water-soluble polysaccharide from *Pinus radiata*, each foamate fraction had a volume of 5 mL. For the batch foaming of the water-soluble holocel-

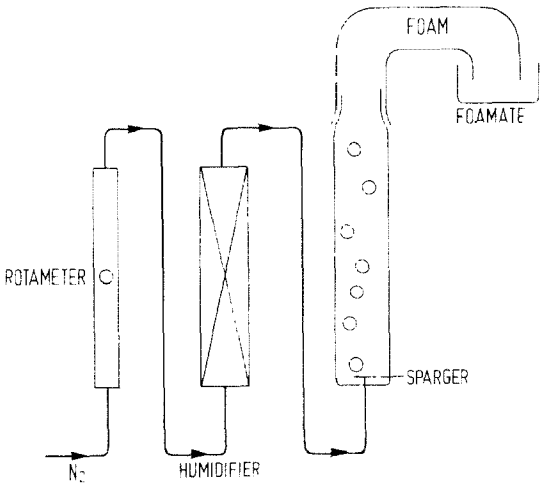

Fig. 9. Batch-foaming apparatus.

lulose and the xylan, the three collapsed, foamate fractions were collected at predetermined time-intervals, rather than on a volumetric basis. The times between fraction collection were 2, 5, and 8 min for the water-soluble holocellulose, and 0.5, 1.0, and 2.0 min for the xylan. The choice of these times depended on the stability and wetness of the foam, as well as on the nitrogen flow rate. The concentrations of the solution foamed, and the nitrogen flow-rates used, are given in Tables I–III.

Continuous-foaming method. — Humidified nitrogen gas was passed through a porous-glass sparger into a foam-fractionation column fitted with a U-tube. The column and U-tube had the same dimensions as for the batch-foaming experiments, and the column was continuously fed, from a constant-head tank containing 2 L of the polysaccharide solution under study, *via* a rotameter-type flow-meter. Gas and feed-solution flow-rates were adjusted to predetermined values. The collapsed foamate and raffinate streams were continuously collected once steady-state operations had been attained. Steady state was assumed to have been reached when the flow rates of both the collapsed foamate and the raffinate streams became constant. This usually occurred after continuous running of the column for 2 h. The feed solution, collapsed foamate, and raffinate were then sampled for analysis.

Quantitative analysis of monosaccharide components. — All samples of feed, foamate, and raffinate streams were evaporated to dryness in a rotary evaporator at 40°. The polysaccharide residue was hydrolyzed with 72% (w/w) sulfuric acid for 1 h at 20° in a stoppered flask. The solution was then diluted to 2.5% acid concentration, refluxed for 4 h, and cooled, *myo*-inositol added as an internal reference, and the solution made neutral with barium carbonate, centrifuged, and the supernatant liquor de-ionized and evaporated to a syrup.

The syrupy hydrolyzate was then converted into the alditol acetates, which

were analyzed in a Shimadzu model GC-4BPF gas chromatograph equipped with flame ionization detectors. The column (1.8 m × 4.8 mm) was packed with 3% of ECNSS-M (liquid phase) on Chromosorb W, AW-HMDS(HP) (100–120 mesh). The column was operated isothermally at 180°. The injection-port temperature was 220°, and that of the detector 210°, and the carrier-gas flow-rate was 60 mL.min^{-1}.

At least six chromatograms of each alditol acetate mixture were prepared, and the ratios of the monosaccharides present were determined by the cut-and-weigh method.

Determination of interfacial area per unit volume (A). — The mean surface area per unit volume of foam bubbles was determined for each experiment as follows. Towards the end of each run, at least three successive photographs were taken of the foam just below the exit from the column, using a 35-mm camera, with Ilford FP4 film, at f/11 and 1/250 s. The framed negatives were projected onto a screen with a slide projector. For each projection, the diameters of at least 20 bubbles were measured, and the mean surface area per unit volume (A) calculated by using the equation given in the Discussion. A typical measurement gave a mean foam-bubble diameter of 1.26 mm (standard deviation 0.14 mm) and values of A were between 44.7 and 46.8 cm^{-1}.

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