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DETERMINATION OF PARTICLE SIZE IN NATURAL LATEX

by

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SUMMARY

The soap titration method of determining average particle sizes in synthetic latices has been modified so as to make it applicable to natural rubber latices.

The method consists essentially in determining the distribution of an added detergent (sodium dodecyl sulphate) between the rubber and aqueous phases at a pH of approximately 6·0, *the total dodecyl sulphate concentration being just sufficient for the formation of micelles in the aqueous phase. The average particle sizes of nine ammoniated latices have been measured, including centrifuged and electrodecanted concentrates, two clonal-field latices and a sample of latex skim.*

INTRODUCTION

Soap titration methods for determining average particle sizes of synthetic latices have been used by a number of workers.[1,2,3] In all cases, the latex (after dilution if necessary) is titrated with a solution of the same soap as that already present as stabiliser, the end-point being the onset of soap micelle formation in the aqueous phase. This occurs, of course, at the critical micellar concentration (c.m.c.) for the soap and several well-known methods for determining the c.m.c. have been used[1,3] for detecting the end-point of the titration. Knowing the c.m.c. and the total amount of soap in the latex at the titration end-point, the quantity of soap adsorbed at the rubber-water interface is found by difference. By assigning a molecular area to the adsorbed soap, the area of rubber-water interface and an average particle diameter can be calculated.

In applying the method to natural rubber latex difficulties arise due to the complex composition of the latex. Thus, inorganic salts and possibly other non-rubber constituents are present in the serum in quantities sufficient to affect significantly the c.m.c. of an added soap and hence the end-point of the titration. This difficulty can be overcome by means of a suitable control experiment (*vide infra*). More important is the fact that the rubber particles in ammoniated latex are stabilised by a film of proteins and fatty acid soap (and probably small amounts of other materials) the composition and concentration of which are seldom known at all accurately. In the modified titration method described below, this difficulty is met by titrating the latex with sodium dodecyl sulphate at a pH value at which the interfacial activity of the dodecyl sulphate is high while that of the fatty acid soaps and proteins is relatively low. By analogy with measurements made at the xylene-water interface,[4] the dodecyl sulphate should be preferentially adsorbed at pH values less than about 8·0.

EXPERIMENTAL METHOD

To determine the amount of sodium dodecyl sulphate adsorbed per unit volume of rubber in a given latex sample, a series of mixtures was prepared from equal weights of the latex by addition of aqueous solutions of sodium dodecyl sulphate, polyvinyl alcohol (present as creaming agent) and acetic acid, in that order, the volume of the mixtures being adjusted by addition of distilled water to give the same final DRC, e.g. 20 per cent. The amount of polyvinyl alcohol and acetic acid used was the same for each mixture, the quantity of acetic acid being sufficient to give a final pH value of 6·0 ± 0·2. The amount of polyvinyl alcohol added should be sufficient to produce a clear, or almost clear, rubber-free serum on allowing the mixture to cream.

The amounts of sodium dodecyl sulphate in the mixtures range from quantities insufficient to cover the rubber particles with a complete monolayer, in which case the dodecyl sulphate in the serum phase will be present as individual molecules, to quantities substantially in excess of that required to cover the particles completely, when most of the detergent in the serum will exist as micelles. If the amount of dodecyl sulphate present is unduly small, i.e. less than about 70 per cent. of that required to form a complete monolayer, the latex is liable to flocculate on addition of the acetic acid solution; this often serves as a rough indication of the end-point. An important precaution to observe in preparing the mixtures is to add the aqueous acetic acid (5 per cent. to 10 per cent. strength) slowly with efficient stirring of the mixture. With each series of mixtures, a control preparation is usually included in which the sodium dodecyl sulphate and acetic acid are omitted.

After allowing the mixtures to cream until a suitable quantity of serum has separated, all the sera (excluding the control) are tested for the presence of detergent micelles. A colorimetric test has been found convenient, using a dilute solution of pinacyanol bromide as indicator. Essentially the same method (spectral dye method) has been used by Klevens[1] for studying the particle sizes of synthetic latices. The presence of detergent micelles in the sera causes a colour change from violet to blue. In distilled water this change occurs at a sodium dodecyl sulphate concentration of 0·2 per cent., i.e. the normal c.m.c., but owing to the presence of salts etc., the colour change in a clear latex serum at pH 6·0 usually occurs at a concentration of approximately 0·04 per cent. of sodium dodecyl sulphate. To find this critical concentration accurately, aliquots of the clear serum from the control experiment are mixed with different amounts of dodecyl sulphate and adjusted to pH 6·0 with acetic acid solution; the required critical concentration is then determined with pinacyanol bromide solution. Since the colour change occurs over a range (even though a small range) of dodecyl sulphate concentration, it is necessary to match approximately the colours of the experimental mixtures with those of the aliquots of the control in order to obtain accurate results. This matching usually requires the preparation of a second series of mixtures in which the total dodecyl sulphate concentration differs by small increments only, i.e. less than 10 per cent. The colour-change at the end-point does not occur instantaneously in latex serum and it is advisable to allow all solutions to "age" for approximately 1 hour, after addition of the dye, before matching colours. A typical example of a particle size determination by the above method is given in Appendix 1.

MOLECULAR ADSORPTION AREA FOR SODIUM DODECYL SULPHATE

Until recently, authors[1,2] have assumed that the molecular area of a normal paraffin chain soap adsorbed at a synthetic rubber—water interface approximates either to that of a close packed insoluble monolayer (21 A^2) or to the cross-sectional area of the molecules in soap micelles (28 A^2). However, experimental determinations of the molecular areas of sodium dodecyl sulphate and potassium myristate adsorbed from aqueous solution at the c.m.c. on to a graphite surface have been obtained by Corrin *et al*,[5] the surface area of the graphite being determined by nitrogen adsorption. Values of 68·3 A^2 for sodium dodecyl sulphate and 56 A^2 for potassium myristate were found. From interfacial tension measurements at the decane-water interface, Cockbain and McMullen[6] obtain a molecular adsorption area (at the c.m.c.) of 49 A^2 for sodium dodecyl sulphate, as calculated from the Gibbs adsorption equation. By comparing soap titration results with electron microscope data Willson, Miller and Rowe[3] obtain an area of 59 A^2 for potassium myristate adsorbed on synthetic rubber particles. In the present work a molecular adsorption area of 60 A^2 has been assumed for sodium dodecyl sulphate, when adsorbed from a solution at the c.m.c.

CALCULATION OF SPECIFIC SURFACE AREA AND AVERAGE PARTICLE DIAMETER

The specific surface area (S), in cm^2, of the rubber, i.e. the average surface area/c.c. of rubber, is obtained from the equation

$$S = \frac{m}{VM} \cdot \frac{N\sigma}{10^{16}} \qquad \ldots\ldots\ldots\ldots(1)$$

where m = grams of sodium dodecyl sulphate adsorbed by V cc. of rubber.
M = molecular weight of sodium dodecyl sulphate
N = Avogadro's number
σ = molecular adsorption area of sodium dodecyl sulphate in A^2.

The area S may be expressed in terms of the volume-surface average diameter (d_{vs}) of the particles, where d_{vs} is the ratio of the cube of the volume average diameter to the square of the surface average diameter

Thus,

$$V = \frac{n\pi}{6}\left(\frac{\sum_i n_i d_i^3}{\sum n_i}\right) = \frac{n\pi d_v^3}{6}$$

$$A = SV = n\pi\left(\frac{\sum_i n_i d_i^2}{\sum_i ni}\right) = n\pi d_s^2$$

Hence,
$$\frac{6}{S} = \frac{d_v^3}{d_s^2} = d_{vs}$$

where n = total number of particles
V = total volume of particles
A = total surface area of particles
d_v = volume average diameter
d_s = surface average diameter
d_{vs} = volume-surface average diameter

RESULTS AND DISCUSSION

Table 1 gives the average specific surface area and the volume-surface average diameter of the following latices, all of which were preserved with ammonia.

Latex 1. Centrifuged concentrate A (DRC 60 per cent.)
,, 2. ,, ,, B (DRC 60 per cent.)
,, 3. Latex 2 purified by creaming
,, 4. Centrifuged concentrate (DRC 61·7 per cent.) } ex-Dunlop Rubber Company Ltd.
,, 5. Electrodecanted concentrate (DRC 60·6 per cent.) }
,, 6. Field latex (DRC 40·5 per cent.)
,, 7. ,, ,, , clone G.1 (DRC 33·6 per cent.)
,, 8. ,, ,, , clone PB·84 (DRC 29 per cent.)
,, 9. Centrifuge skim (total solids = 8·7 per cent.) concentrated by creaming.

TABLE 1

PARTICLE SIZE DATA FOR AMMONIA PRESERVED LATICES

Latex	Detergent adsorbed per c.c. rubber (mg.)	Specific Surface Area(s) (cm²)	Volume-surface average diameter (d_{vs}) in microns
1	6·6	8·3 × 10⁴	0·72
2	9·5	11·9 × 10⁴	0·51
3	8·9	11·2 × 10⁴	0·54
4	6·4	8·0 × 10⁴	0·75
5	11·1	13·9 × 10⁴	0·43
6	15·0	18·9 × 10⁴	0·32
7	10·2	12·9 × 10⁴	0·46
8	16·1	20·4 × 10⁴	0·29
9	41·2	52 × 10⁴	0.12

Latices 1 and 2 were two different commercial samples. Latex 3 was prepared by creaming latex 2 with polyvinyl alcohol solution (sufficient to give a clear serum) so that the original serum components were diluted 17 times. The results with latices 2 and 3 agree sufficiently well to show that large variations in the concentration of natural serum components do not affect appreciably the accuracy of the method. Samples 4 and 5 were kindly provided by the Dunlop Rubber Company Ltd.; these two latices were prepared from the same field latex, but were concentrated by different processes, as described above. Latex 6 was of unknown origin but corresponds fairly closely in average particle size to the Pb.84 latex. The Glenshiel 1 latex is of relatively large particle size. In general, the particle sizes are in the sequence which would be expected from the methods of treating the original field latices, and it seems safe to conclude that this method gives reliable relative surfaces areas.

The most direct test of the validity of the method in an absolute sense involves comparison of the results with particle sizes determined directly by means of an electron microscope. Preliminary measurements of this kind, for which we are indebted to Dr. Cosslett, of the Physics Dept., Cambridge University, were made on latex 7. Our analysis of his electron micrographs indicates that the true specific surface area for this latex is probably slightly less than the value of S given in Table 1. Further comparisons with electron microscope data are required, however, before attempting to assess the absolute accuracy of the soap titration method.

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APPENDIX 1. DETERMINATION OF SPECIFIC SURFACE AREA(S) OF CENTRIFUGED LATEX (DRC 60·0 PER CENT.)

Four samples of the latex (of density 0·95), each weighing 20·0 gm., were taken and to each sample was added with mechanical stirring a different volume of a 2·0 per cent. solution (w/v) of pure sodium dodecyl sulphate,* viz. (*a*) 3·0 ml., (*b*) 5·0 ml., (*c*) 7·0 ml., (*d*) 9·0 ml. To each sample was then added 25·0 ml. of 4 per cent. polyvinyl alcohol solution followed by 9·5 ml. of 5 per cent. acetic acid; the latter was added slowly with efficient stirring. The volume of each sample was finally made up to 65·0 ml. with distilled water, the volume of the 20·0 gm. of latex being known from an approximate density determination. The pH of samples (*a*) and (*d*) was checked with a glass electrode to confirm that the pH was 6·0 ± 0·2. The samples were allowed to cream for 24 hours in separating funnels.

To 5.0 ml. of the clear serum from each sample, 0·3 ml of a 0·005 per cent. solution of pinacyanol bromide in water was added and the 4 samples were then allowed to stand for 1 hour. The change in colour from violet to blue occurred between samples (*b*) and (*c*).

Another series of mixtures was therefore prepared, exactly as above, containing (*f*) 5.0 ml., (*g*) 5.4 ml., (*h*) 5.8 ml., (*i*) 6.2 ml., (*j*) 6·6 ml., and (*k*) 7·0 ml. of 2·0 per cent. sodium dodecyl sulphate solution. A "blank" sample (1) was also prepared, containing 40 gm. latex, 50 ml. of 4 per cent. polyvinyl alcohol solution and 40 ml. distilled water. All samples were allowed to cream for 24 hours (the volume of the polyvinyl alcohol solution in sample (1) can be increased at the expense of the distilled water if it is evident that an almost clear serum is not being obtained).

To 5·0 ml. portions of the almost clear serum from the blank experiment, 0·06, 0·08, 0·10, 0·12, 0·14 and 0·16 ml. of 2·0 per cent. sodium dodecyl sulphate solution were added. The pH of each was then reduced

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*It is suggested that the following criteria of purity would be suitable:—Moisture less than 1 per cent., inorganic matter less than 1 per cent.; in addition, the critical micellar concentration of the detergent in distilled water, as determined by the pinacyanol bromide (or chloride) method, should be between 0·15 per cent. and 0·21 per cent.

to 6·0 ± 0·2 by addition of ca. 0·2 ml. of 25 per cent. acetic acid, followed by the addition of 0·3 ml. of a 0·005 per cent. solution of pinacyanol bromide (more reproducible results are obtained if the dye solution is freshly prepared, i.e. not more than about 24 hours old). At the same time, so far as practicable, 5·0 ml. aliquots of the clear serum from each of the samples (*f*) to (*k*) were taken and 0·3 ml. of the same pinacyanol bromide solution were added. All aliquots were then allowed to stand 1 hour.

The maximum colour change in the aliquots from the blank experiment (1) occurred between 0·10 and 0·14 ml. of the added dodecyl sulphate solution.

∴ critical micellar concentration of the dodecyl sulphate in the acidified serum of sample (1) $= \frac{0{\cdot}12}{5{\cdot}6} \times 2{\cdot}0$ per cent. $= 0{\cdot}04$ per cent.

The corresponding colour change in the aliquots from samples (*f*) to (*k*) occurred in sample (*g*). The titration end-point was therefore taken as 5·4 ml. of 2·0 per cent. sodium dodecyl sulphate.

CALCULATION OF SPECIFIC SURFACE AREA (S)

In all experiments, the density of the rubber particles is taken as 0·91,

Hence, 20·0 gm. latex (60·0 per cent. DRC) contain $\frac{12{\cdot}0}{0{\cdot}91} = 13{\cdot}2$ cc. rubber

∴ Composition of sample (*g*) = 13·2 cc. rubber (v) + (65·0 — 13·2) cc. of aqueous phase.

Wt. of sodium dodecyl sulphate added at titration end-point $= \frac{2{\cdot}0}{100} \times 5{\cdot}4$ gm., of which $\frac{0{\cdot}04}{100} \times 51{\cdot}8$ gm. $= 0{\cdot}021$ gm. remain in the aqueous phase.

∴ wt of dodecyl sulphate adsorbed (m) $= 0{\cdot}108 - 0{\cdot}021$
$= 0{\cdot}087$ gm.

Thus, if M = molecular weight (288) of sodium dodecyl sulphate, N = Avogadro's number and σ = molecular adsorption area of the detergent, assumed to be 60A², the surface area S per cc. of rubber is given by:—

$$S = \frac{m}{MV} \cdot \frac{N\sigma}{10^{16}} = \frac{0{\cdot}087 \times 6{\cdot}06 \times 10^{23} \times 60}{13{\cdot}2 \times 288 \times 10^{16}}$$

$$= 8{\cdot}3 \times 10^{4}\ \text{cm}^2$$

REFERENCES

1. Klevens, *J. Colloid Sci.*, 1947, **2**, 365.
2. Maron, Elder and Ulevitch, Communication to Am. Chem. Soc. Meeting, New York City, 19th September, 1947.
3. Willson, Miller and Rowe, *J. Phys. & Colloid Chem.*, 1949, **53**, 357.
4. Powney and Addison, *Trans. Farady Soc.*, 1937, **33**, 1243; 1938, **34**, 356.
5. Corrin, Lind, Roginsky and Harkins, *J. Colloid Sci.*, 1949, **4**, 485.
6. Cockbain and McMullen, *Trans. Faraday Soc.*, 1951, **47**, 322.

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