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(57) Abrégé/Abstract:
A paper making process comprises: (a) adding to an aqueous paper furnish containing pulp and optionally inorganic filler a water-soluble polyparticulate polysilicate microgel and a water-soluble cationic polymer, and (b) forming and drying the product of step (a), wherein the microgel has an average particle size in the range 20 to 250 nm and a surface area in excess of 1000 m^2/g. The polysilicate microgel is preferably a polyaluminosilicate, especially one having a mole ratio of alumina : silica of between 1:10 and 1:1500. The use of such microgels leads to improved drainage and retention characteristics.

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A paper making process comprises: (a) adding to an aqueous paper furnish containing pulp and optionally inorganic filler a water–soluble polyparticulate polysilicate microgel and a water–soluble cationic polymer, and (b) forming and drying the product of step (a), wherein the microgel has an average particle size in the range 20 to 250 nm and a surface area in excess of 1000 m^2/g. The polysilicate microgel is preferably a polyaluminosilicate, especially one having a mole ratio of alumina : silica of between 1:10 and 1:1500. The use of such microgels leads to improved drainage and retention characteristics.

PAPER MAKING PROCESS

This invention relates to processes for making paper, and is especially concerned with such processes which involve the use of water soluble polysilicate microgels, especially polyaluminosilicate microgels and non-aluminized polysilicate microgels, as retention and drainage aids.

BACKGROUND OF THE INVENTION

The formation of water soluble polysilicate microgels and their use in papermaking is known. U.S. 4,954,220 relates to polysilicate microgels and their use in papermaking. The December 1994 Tappi Journal (vol. 77, No. 12) at pages 133-138 contains a review of such products and their uses. U.S. 5,176,891 discloses a process for the production of polyaluminosilicate microgels involving the initial formation of a polysilicic acid microgel followed by reaction of the polysilicic acid microgel with an aluminate to form the polyaluminosilicate. The use of the polyaluminosilicate microgels as improved retention and drainage agents in papermaking is also disclosed. U.S. 5,127,994 discloses a process for the production of paper by forming and dewatering a cellulosic fiber suspension in the presence of three compounds: an aluminum salt, a cationic polymeric retention agent and polysilicic acid.

The polyaluminosilicate microgel process disclosed in U.S. 5,176,891 comprises three steps, namely (1) the acidification of a water solution of an alkali metal silicate to form polysilicic acid microgel, (2) addition of a water soluble aluminate to the polysilicic acid microgel

to form the polyaluminosilicate and (3) dilution to stabilize the product against gelation. There is a necessary ageing period involved following the acidification step during which the silicic acid first formed polymerizes to linear polysilicic acid and then to the microgel structure which is critical to the performance of the polyaluminosilicate products. The products are described as having a surface area of greater than 1000 square meters per gram, a surface acidity of greater than about 0.6 milliequivalents per gram and an alumina/silica mole ratio of greater than 1:100, preferably between 1:25 and 1:4.

WO 95/25068 describes an improvement over the process described in US 5,176,891 in that it combines the acidification and alumination steps. An unexpected and important benefit resulting is that the ageing period required for microgel formation to occur is significantly reduced. The polyparticulate polyaluminosilicate products produced by the process of that invention have good activity as retention and drainage agents in papermaking immediately on formation (no ageing period) and they reach their optimum performance in significantly less time than those prepared by previous methods. Ageing periods required for product formation are avoided or minimized whenever possible in paper making since they require additional or oversized equipment and are known to give rise to problems such as products of uneven quality. Any reduction in the ageing period is thus an improvement in the process of paper making and in product quality.

SUMMARY OF THE INVENTION

An important aspect of the process described in WO 95/25068 is the addition of a water soluble aluminum salt to an acid used for the acidification of an alkali metal silicate solution. This way, hydrated aluminum hydroxide is produced at the same time as silicic acid and thus, during the polymerization of silicic acid to polysilicic acid and formation of a polyparticulate microgel, aluminum hydroxide is incorporated directly into the polymer with the attendant formation of polyaluminosilicate. This process can produce useful polyaluminosilicates (PAS) over a wide range of compositions having alumina/silica mole ratios ranging from approximately 1:1500 to 1:10 but generally about 1:1000 or less preferably 1:750 to 1:25 and most preferably 1:500 to 1:50. Because of the low alumina/silica ratio, the total surface acidity of the polyaluminosilicates does not differ significantly from that of non-aluminated polysilicate microgels. At the same time an anionic charge is maintained into lower pH ranges than is observed with non-aluminated polysilicic acid.

According to one aspect of the invention, there is provided a process for making paper comprising the steps of:

(a) adding to an aqueous paper furnish containing pulp and optionally inorganic filler, up to 1% by weight, based on the dry weight of the furnish, of a water soluble polyparticulate polyaluminosilicate microgel having a mole ratio of alumina:silica of between 1:10 and

1:1500 prepared by a process comprising the steps of

(i) acidifying an aqueous solution of an alkali metal silicate containing 0.1-6% by weight of SiO_2, to a pH of 2-10.5 by adding an aqueous acidic solution containing sufficient aluminium salt to provide the mole ratios; and

(ii) adjusting the pH of the product of step (i) to between 1-4 before, after or concurrently with a dilution step, but prior to gelation, to achieve a SiO_2 content of ≤ 5% by weight;

and at least approximately 0.001% by weight, based on the dry weight of the furnish, of a water soluble cationic polymer;

wherein the microgel has an average particle size of 20-250 nm and a surface area in excess of 1000 m^2/g; and

(b) forming and drying the product of step (a)

According to another aspect of the invention, there is provided a process for the preparation of a water-soluble polyparticulate polyaluminosilicate microgel having a mole ratio of alumina:silica of between 1:10 and 1:1500, an average microgel particle size of 20-250 nm and a surface area in excess of 1000 m^2/g; comprising the steps of

(i) acidifying an aqueous solution of an alkali metal silicate, wherein the solution contains 0.1-6% by weight of SiO_2, to a pH of 2-10.5 by adding an aqueous acidic solution containing sufficient aluminum salt to provide the mole

ratios; and

(ii) adjusting the pH of the product of step (i) to between 1-4 before, after or concurrently with a dilution step, but prior to gelation, to achieve a SiO_2 content of ≤ 5% by weight.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph showing results of Canadian Standard Freeness tests plotted against microgel size for a first papermaking formulation.

Figure 2 is a graph showing ash retention (%) plotted against microgel size for the first papermaking formulation.

Figure 3 is a graph showing results of Canadian Standard Freeness tests plotted against microgel size for a second papermaking formulation.

Figure 4 is a graph showing results of Canadian Standard Freeness tests plotted against microgel size for a third papermaking formulation.

Figure 5 is a graph showing results of Canadian Standard Freeness tests plotted against microgel size for a fourth papermaking formulation.

DETAILED DESCRIPTION OF THE INVENTION

The process of WO 95/25068 can be carried out as a two-step process comprising

(a) acidifying an aqueous solution of an alkali metal silicate containing 0.1-6% by weight of SiO_2 to a pH of 2-10.5 by using an aqueous acidic solution containing an aluminum salt; and

(b) diluting the product of step (a) with water prior to gelation to a SiO_2 content of ≤ 2% by weight.

Optionally, after the acidification step, an ageing step can be employed to improve product performance further.

Such an ageing period is not required and is somewhat counter to the benefit gained from the process, a reduction in the time required for the polyaluminosilicate products to reach maximum activity.

Any water soluble silicate salt can be used in the process, alkali metal silicates such as sodium silicate being preferred. As an example, sodium silicate, $Na_2O:3.2\ SiO_2$ by weight, can be used.

Any acid with a pKa less than about 5 can be used. Inorganic mineral acids are preferred over organic acids; sulfuric acid is the most preferred.

Any aluminum salt can be used which is soluble in the acid used. Suitable choices are aluminum sulfate, chloride, nitrate and acetate. Basic salts such as sodium aluminate and chlorohydrol, $Al(OH)_2Cl$ can also be used. If alkali metal aluminates are used, they can be first converted to an aluminum metal salt by reaction with the acid.

To carry out the process of WO 95/25068, a dilute aqueous solution of an alkali metal silicate, containing from about 0.1-6 wt% SiO_2, preferably about 1-5 wt% SiO_2 and most preferably 2-4 wt%, is rapidly mixed with a dilute aqueous solution of an acid containing a dissolved aluminum salt so as to produce a solution within a pH range of about 2-10.5. A more preferred pH range is from 7-10.5 with the most preferred range being pH 8-10. Suitable acid concentrations range from 1-50wt% although both lower and higher concentrations can be used provided adequate mixing is employed. Generally a concentration of about 20wt% acid is preferred. The amount of aluminum salt dissolved in the acid solution can vary from about 0.1 wt% up to the limit of solubility of the salt in the acid.

The mole ratio of Al_2O_3/SiO_2 in the polyaluminosilicate microgels produced by this process can vary widely from about 1:500 to 1:10 depending upon the concentration of the acid used, the amount of aluminum salt dissolved in the acid and the pH of the resulting partially neutralized silicate solution. Acidification into lower pH ranges requires the use of more acid and can result in the production of polyaluminosilicates containing higher alumina/silica mole ratios. Solubility data of an $Al_2(SO_4)_3$-H_2SO_4-H_2O system (Linke, "Solubility of Inorganic Compounds", 4th Ed. 1958, Vol 1) provide a basis for calculating the maximum Al_2O_3/SiO_2 ratios obtainable in polyaluminosilicates (when using $Na_2O:3.2SiO_2$ as the silicate) using sulfuric acid solutions containing from 10-50 wt% acid, saturated with aluminum sulfate, for the acidification of a silicate solution to pH9. (At this pH, approximately 85% of the alkalinity of $Na_2O:3.2SiO_2$ is neutralized.)

H_2SO_4 Wt%	$Al_2(SO_4)_3$ Wt%	Polyaluminosilicate Al_2O_3/SiO_2 mole ratio
10	19.6	1/22
20	13.3	1/32
30	8.1	1/61
40	4.3	1/138
50	2.5	1/283

It has been found that the process of preparing PAS microgels can preferably be carried out using an acid solution containing about 20 wt% sulfuric acid and from 1-6 wt% of dissolved aluminum sulfate. Using such acid solutions over the preferred pH range of 8-10 (representing approximately 95-60 wt% neutralization of $Na_2O:3.2SiO_2$,

polyaluminosilicate microgels with Al_2O_3/SiO_2 mole ratios of from about 1:35 to 1:400 can be obtained. Within the preferred concentration and pH ranges, the polyaluminosilicate solutions are clear and, after dilution to about 0.5 wt% SiO2, retain their activity in flocculation processes for about 24 hours.

While the process described in WO 95/25068 produces PAS microgels which are of particular advantage in papermaking, it has now surprisingly been found that even better results can be obtained with non-aluminized or polyaluminosilicate microgels having an average particle (microgel) size or dimension between 20 and 250 nanometers. Accordingly the present invention provides a papermaking process which comprises

(a) adding to an aqueous paper furnish containing pulp and optionally inorganic filler a water-soluble polyparticulate polysilicate microgel having an average particle size of 20 - 250 nm and a surface area in excess of 1000 m^2/g, and a water-soluble cationic polymer; and

(b) forming and drying the product of step (a).

The microgels used in this invention are preferably those which have an average particle size in the range 40 - 250 nm, more preferably 40 - 150 nm, and most preferably 50 - 100. They may be non-aluminised polysilicate microgels or PAS microgels made, for example, by the two-step process described in WO 95/25068 wherein following the acidification step the product is aged, for a time depending on the process conditions (i.e. pH, silica

concentration, aluminium concentration, temperature) selected. Ageing times in the range 4 to 40 minutes, for example 5 to 30 minutes, may normally be used to produce the desired particle size. For example, an ageing time of the order of 15 minutes can produce a microgel having an average particle size of about 100 nm.

The surface area of the microgels is at least 1000 m^2 per gram, preferably 1360 to 2720 m^2 per gram.

The microgels are preferably polyaluminosilicate microgels, especially those having a mole ratio of alumina: silica of between 1:10 and 1:1500. The activity of the polyaluminosilicate microgels can be further improved and this activity can be maintained for longer periods of time by adjusting the microgel pH to about pH 1 to 4 before, after or concurrently with the dilution step. Another advantage of adjusting the microgel pH to about pH 1-4 is that the microgels can be stored at higher silica concentrations. Thus it can be possible to eliminate the dilution step completely depending on the silica concentration during the addition of the aqueous acidic solution of an aluminum salt. The adjustment of pH to between about 1-4 permits storing polyaluminosilicate microgels at up to 4-5 weight %. Any acid that will lower the microgel pH to about pH 1-4 can be used. Inorganic mineral acids are preferred over organic acids; sulfuric acid is the most preferred.

Thus, in accordance with a preferred embodiment of the invention a process for making paper comprises the steps of

(a) adding to an aqueous paper furnish containing pulp and optionally inorganic filler, up to 1%, preferably 0.01-1%, by weight, based on the dry weight of the furnish, of a water soluble polyparticulate polyaluminosilicate microgel having a mole ratio of alumina:silica of between 1:10 and 1:1500 prepared by a process comprising the steps of

(i) acidifying an aqueous solution of an alkali metal silicate containing 0.1-6% by weight of SiO_2 to a pH of 2-10.5 by adding an aqueous acidic solution containing sufficient aluminum salt to provide said mole ratios; and

(ii) adjusting the pH of the product of step (i) to between 1-4 before, after or concurrently with a dilution step, but prior to gelation, to achieve a SiO_2 content of $\leq$ 5% by weight;

and at least approximately 0.001 % by weight, based on the dry weight of the furnish, of a water soluble cationic polymer;

wherein the microgel has an average particle size of 20-250 nm; and

(b) forming and drying the product of step (a).

The adjustment of the pH in step (a)(ii) above is preferably a reduction of the pH, the acidification in step (a)(i) preferably producing a pH of 7 to 10.5, more preferably 8 to 10, and most preferably 8 to 8.5. The solution of alkali metal silicate preferably contains 2 to 3% SiO_2, by weight.

The polysilicates used in this invention can be utilized in a wide variety of flocculation processes and act as retention and drainage agents in paper making (used in the amount of up to 1%, preferably 0.01-1%, by weight, based on the dry weight of the paper furnish). They may be employed in combination with cationic polymers such as cationic starch, cationic polyacrylamide and cationic guar. These are described in U.S. 4,927,498 and U.S. 5,176,891. Such (water soluble) cationic polymers are present to the extent of at least about 0.001 weight % based on the dry weight of the furnish. Thus, the invention also provides a process for making paper comprising the steps of

(a) adding to an aqueous paper furnish containing pulp and optionally inorganic filler a water soluble polyparticulate polyaluminosilicate microgel consisting essentially of

(i) microgels having mole ratios of alumina:silica between 1:25 and 1:1500 wherein aluminum ions are present both intra- and inter-particle and wherein the particles in the microgel have diameters of 1-2 nm; and

(ii) water such that the microgels are present at $\leq$ 5% by weight based on SiO_2 content and at a pH of 1-4;

and at least approximately 0.001% by weight based on the dry weight of the furnish of a water soluble cationic polymer;

wherein the microgel has an average particle size of 20-250 nm; and

(b) forming and drying the product of step (a).

Anionic polymers such as anionic polyacrylamide, anionic starches, anionic guar, anionic polyvinyl acetate and carboxymethylcellulose and its derivatives can also be used in conjunction with the polysilicate microgels and cationic polymers with beneficial results. Depending on the papermaking conditions, various other chemicals can also be employed in conjunction with the polysilicate microgels and high molecular weight cationic polymers. In systems containing large amounts of anionic trash, for example, low molecular weight, high charge-density cationic polymers such as polyethyleneimine, polydiallyldimethylammonium chloride and amine-epichlorohydrin condensation products can be added to achieve a charge balance within the system more effectively and obtain improved results. Additional quantities of aluminum salts beyond those contained in the acidic solution, such as alum and sodium aluminate, can also be added for improved results in certain circumstances. These can be added to the papermaking furnish either by premixing with the polysilicate microgels of this invention or by separate addition.

The following Examples are given for the purpose of illustrating, but not limiting, the invention.

EXAMPLE 1

A polyaluminosilicate (PAS) solution was prepared by mixing 21 g of 3.22 ratio sodium silicate containing 28.5% SiO_2 with 260 grams of deionized water. To the resulting 2.1

wt% SiO_2 solution was added 9.84 ml of 5N H_2SO_4 solution containing 0.052 g of $Al_2(SO_4)_3.17H_2O$ to give a pH of 8.6. Aliquots of the resulting 2 wt% PAS solution (SiO_2 basis) were diluted and stabilized at 0.125 wt% PAS (SiO_2 basis) at pH 2.5 by diluting with 0.0085N H_2SO_4 solution at various times.

Average microgel sizes of the 0.125 wt% PAS (SiO_2 basis) samples were determined using a Brookhaven Instrument light scattering goniometer, model BI-200SM. Measurements were conducted at room temperature using an argon-ion laser with a wavelength of 488 nm operating at 200 mW power. Light scattering intensity measurements were made at different angles and the data were analyzed using a Zimm plot. Average microgel particle sizes were obtained from particle size distribution.

Performance of the 0.125 wt% PAS solutions as a papermaking retention and drainage aid was determined by conducting Canadian Standard Freeness tests using a 0.3 wt% consistency, pH 8, bleached Kraft furnish containing 35% hardwood, 35% softwood and 30% precipitated calcium carbonate. Product performance was tested by adding to the paper furnish 20 lb/t (dry furnish basis) of BMB-40 cationic potato starch 15 seconds prior to the addition of 2 lb/t of the PAS solutions (SiO_2 basis). Mixing was conducted in a Britt Jar at 750 rpm and the flocculated furnish was then transferred to a Canadian Standard Freeness tester and drainage measurements were made. Freeness results (in ml) and average silica particle (microgel) size (in nanometers) versus dilution time are shown in Table 1 below.

Retention was also determined using a Britt jar at 750 rpm, by adding to the paper furnish 20 lb/ton BMB-40 (see above) 15 seconds prior to the addition of 2 lb/ton of the PAS solutions (SiO_2 basis). After a further 15 seconds agitation, draining commenced. Five seconds later white water began to be collected, and this continued until 100 mls of white water had been collected. This was filtered through a glass fibre filter, the solids were dried and then burnt. The resulting ash was weighed, and the ash retention was calculated. The results are also given in Table 1. The results are also shown graphically in Figure 1, which shows Freeness plotted against microgel size; and in Figure 2, which is a graph of Ash Retention against microgel size.

The performance of the PAS solutions was also tested (using the above Canadian Standard Freeness test procedure) in different papermaking formulations, namely

(i) wherein 10 lb/t of BMB-40 cationic potato starch was added to the paper furnish 15 seconds prior to the addition of 0.25 lb/t of cationic Percol 182, followed 15 seconds later by the addition of 1 lb/t of the PAS solutions;

(ii) wherein 15 lb/t of BMB-40 cationic potato starch was added to the paper furnish 15 seconds prior to the addition of 0.25 lb/t of alum (Al_2O_3 basis), followed 15 seconds later by the addition of 1 lb/t of the PAS solutions;

(iii) wherein 20 lb/t of BMB-40 cationic potato starch was added to the paper furnish 15 seconds prior to the

addition of 0.25 lb/t of anionic Percol 90L, followed 15 seconds later by 1 lb/t of the PAS solutions.

The results of these three tests are shown graphically in Figures 3 to 5, which show Freeness plotted against microgel size for tests (i) to (iii) respectively.

TABLE 1

Dilution Time	Freeness	Average Particle Size	Ash Retention
(minutes)	(ml)	(nm)	%
0.5	580	8.1	21
1	615	11.9	23
2	640	18.1	31
5	660	41.0	31
15	660	107.7	35
30	640	250	28
35	610	357	26
37	610	530	23
39	595	838	23

EXAMPLE 2

A PAS solution was prepared by mixing 21 g of 3.22 ratio sodium silicate containing 28.5% SiO_2 with 260 grams of deionized water. To the resulting 2.1 wt% SiO_2 solution was added 8.75 ml of 5N H_2SO_4 solution containing 0.80 g of $Al_2(SO_4)_3.17H_2O$ to give a pH of 8.5. Aliquots of the resulting 2 wt% PAS solution (SiO_2 basis) were diluted and stabilized at 0.125 wt% PAS (SiO_2 basis) at pH 2.0 by diluting with 0.0085N H_2SO_4 solution at various times.

Average microgel sizes of the 0.125 wt% PAS (SiO_2 basis) samples were determined as above, and Freeness tests were conducted as described in Example 1. The results are given in Table 2.

TABLE 2

Dilution Time	Freeness	Average Particle Size
(mins)	(ml)	(nm)
0.5	580	4.4
5	650	43.5
17	620	296

EXAMPLE 3

A non-aluminised polysilicate (PS) solution was prepared by mixing 21 g of 3.22 ratio sodium silicate containing 28.5% SiO_2 with 260 grams of deionized water. To the resulting 2.1 wt% SiO_2 solution was added 10 ml of 5N H_2SO_4 solution. Aliquots of the resulting 2 wt% PS solution (SiO_2 basis) were diluted and stabilized at 0.125 wt% PS (SiO_2 basis) at pH 2.5 by diluting with 0.0085N H_2SO_4 solution at various times.

Average microgel sizes were determined and Freeness measurements made as in Example 1. The results are given in Table 3.

TABLE 3

Dilution Time	Freeness	Average Particle Size
(mins)	(ml)	(nm)
0.5	550	3.7
15	640	40.5
30	630	60.5
420	590	201

As can be seen from the data, microgel size in the range of this invention affords the best performance in paper making (as measured by both freeness and ash retention).

CLAIMS:

1. A process for making paper comprising the steps of :

(a) adding to an aqueous paper furnish containing pulp and optionally inorganic filler, up to 1% by weight, based on the dry weight of the furnish, of a water soluble polyparticulate polyaluminosilicate microgel having a mole ratio of alumina:silica of between 1:10 and 1:1500 prepared by a process comprising the steps of

(i) acidifying an aqueous solution of an alkali metal silicate containing 0.1-6% by weight of SiO_2, to a pH of 2-10.5 by adding an aqueous acidic solution containing sufficient aluminium salt to provide said mole ratios; and

(ii) adjusting the pH of the product of step (i) to between 1-4 before, after or concurrently with a dilution step, but prior to gelation, to achieve a SiO_2 content of $\leq 5\%$ by weight;

and at least approximately 0.001% by weight, based on the dry weight of the furnish, of a water soluble cationic polymer,

wherein the microgel has an average particle size of 20-250 nm and a surface area in excess of 1000 m^2/g; and

(b) forming and drying the product of step (a).

2. A process as claimed in claim 1 comprising ageing the product of step (a) for from 4 to 40 minutes.

3. A process as claimed in claim 2 comprising ageing the product of step (a) for from 5 to 30 minutes.

4. The process of any one of claims 1 to 3 wherein there is an additional amount of aluminium compound added to the paper furnish.

5. The process of any one of claims 1 to 4 wherein there is an anionic polymer added to the paper furnish.

6. A process as claimed in any one of claims 1 to 5 wherein the acidification in step (i) produces a pH of 7 to 10.5.

7. A process as claimed in claim 6 wherein the acidification in step (i) produces a pH of 8 to 10.

8. A process as claimed in claim 7 wherein the acidification in step (i) produces a pH of 8 to 8.5.

9. A process as claimed in any one of claims 1 to 8 wherein the solution of alkali metal silicate contains 2 to 3% SiO_2 by weight.

10. A process as claimed in any one of claims 1 to 9 wherein the microgel has an average particle size in the range 40 to 250 nm.

11. A process as claimed in any one of claims 1 to 10 wherein the microgel has an average particle size in the range 40 to 150 nm.

12. A process as claimed in claim 11 wherein the microgel has an average particle size in the range 50 to 150 nm.

13. A process as claimed in claim 12 wherein the microgel has an average particle size in the range 50 to 100 nm.

14. A process as claimed in any one of claims 1 to 13 in which the microgel has a surface area of 1360 to 2720 m^2 per gram.

15. A process for the preparation of a water-soluble polyparticulate polyaluminosilicate microgel having a mole ratio of alumina:silica of between 1:10 and 1:1500, an average microgel particle size of 20-250 nm and a surface area in excess of 1000 M^2/g; comprising the steps of

(i) acidifying an aqueous solution of an alkali metal silicate, wherein the solution contains 0.1-6% by weight of SiO_2, to a pH of 2-10.5 by adding an aqueous acidic solution containing sufficient aluminum salt to provide said mole ratios; and

(ii) adjusting the pH of the product of step (i) to between 1-4 before, after or concurrently with a dilution step, but prior to gelation, to achieve a SiO_2 content of ≤ 5% by weight.

16. A process as claimed in claim 15 wherein the acidification in step (i) produces a pH of 7 to 10.5.

17. A process as claimed in claim 16 wherein the acidification in step (i) produces a pH1 of 8 to 10.

18. A process as claimed in any one of claims 15 to 17 wherein the microgel has an average particle size in the range 40 to 250 nm.

19. A process as claimed in claim 18 wherein the microgel has an average particle size in the range 50 to 150 nm.

20. A water soluble polyparticulate polyaluminosilicate microgel in water consisting essentially of a microgel obtained according to any one of claims 15 to 19.

FIG. 1

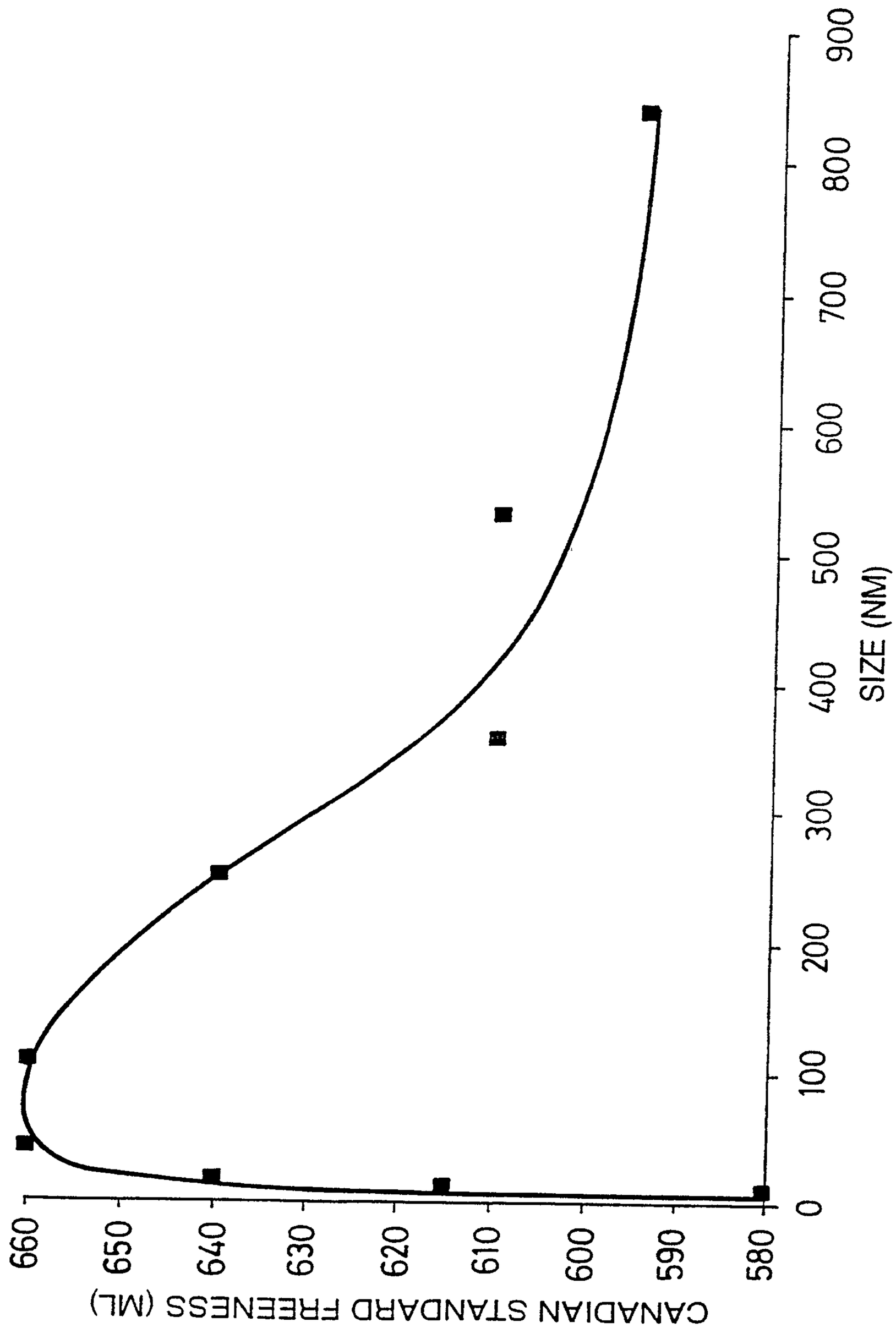

CANADIAN STANDARD FREENESS (ML)
660
650
640
630
620
610
600
590
580
0
100
200
300
400
500
600
700
800
900
SIZE (NM)

FIG. 2

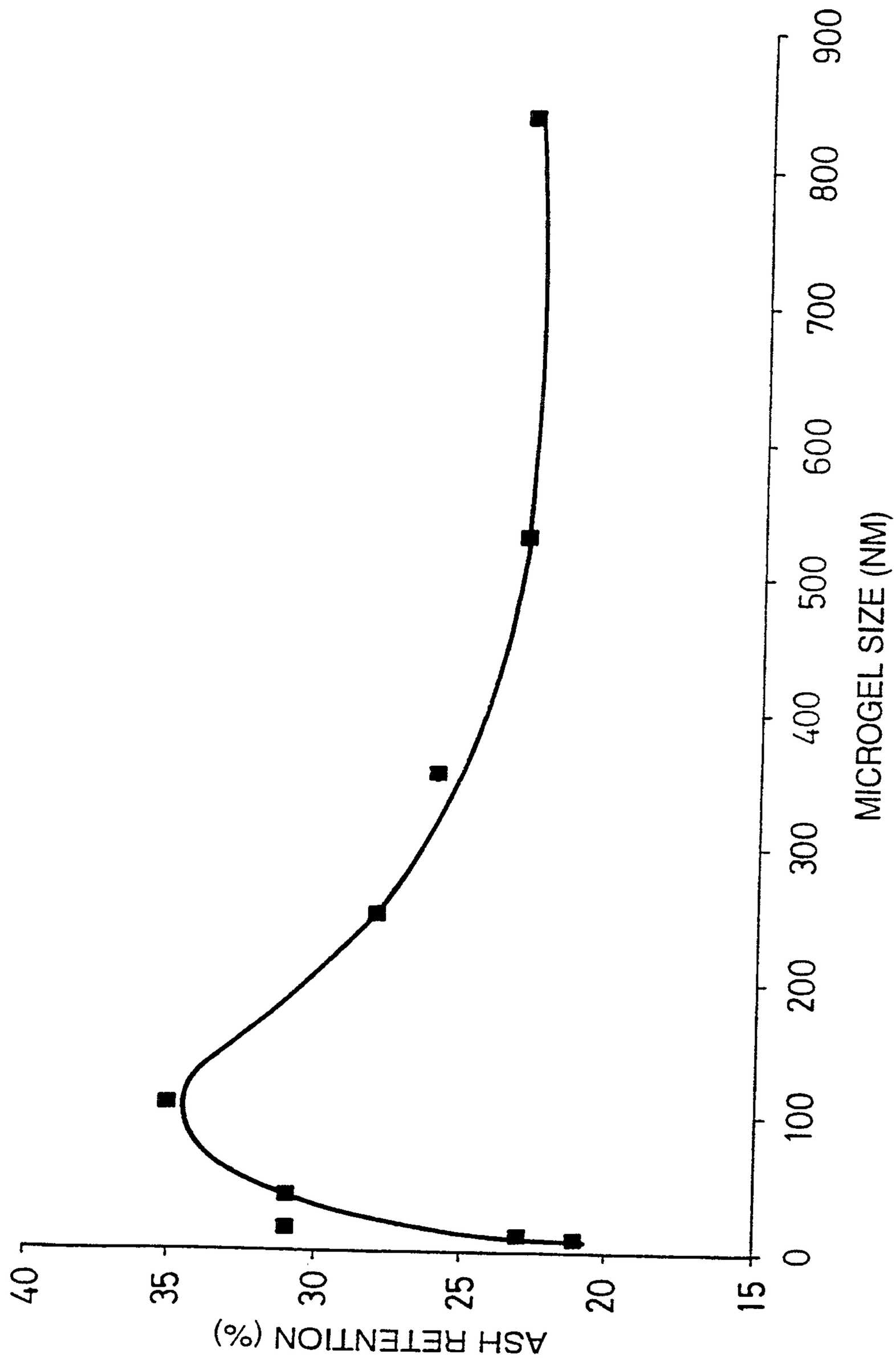

ASH RETENTION (%)
40
35
30
25
20
15
0
100
200
300
400
500
600
700
800
900
MICROGEL SIZE (NM)

FIG. 3

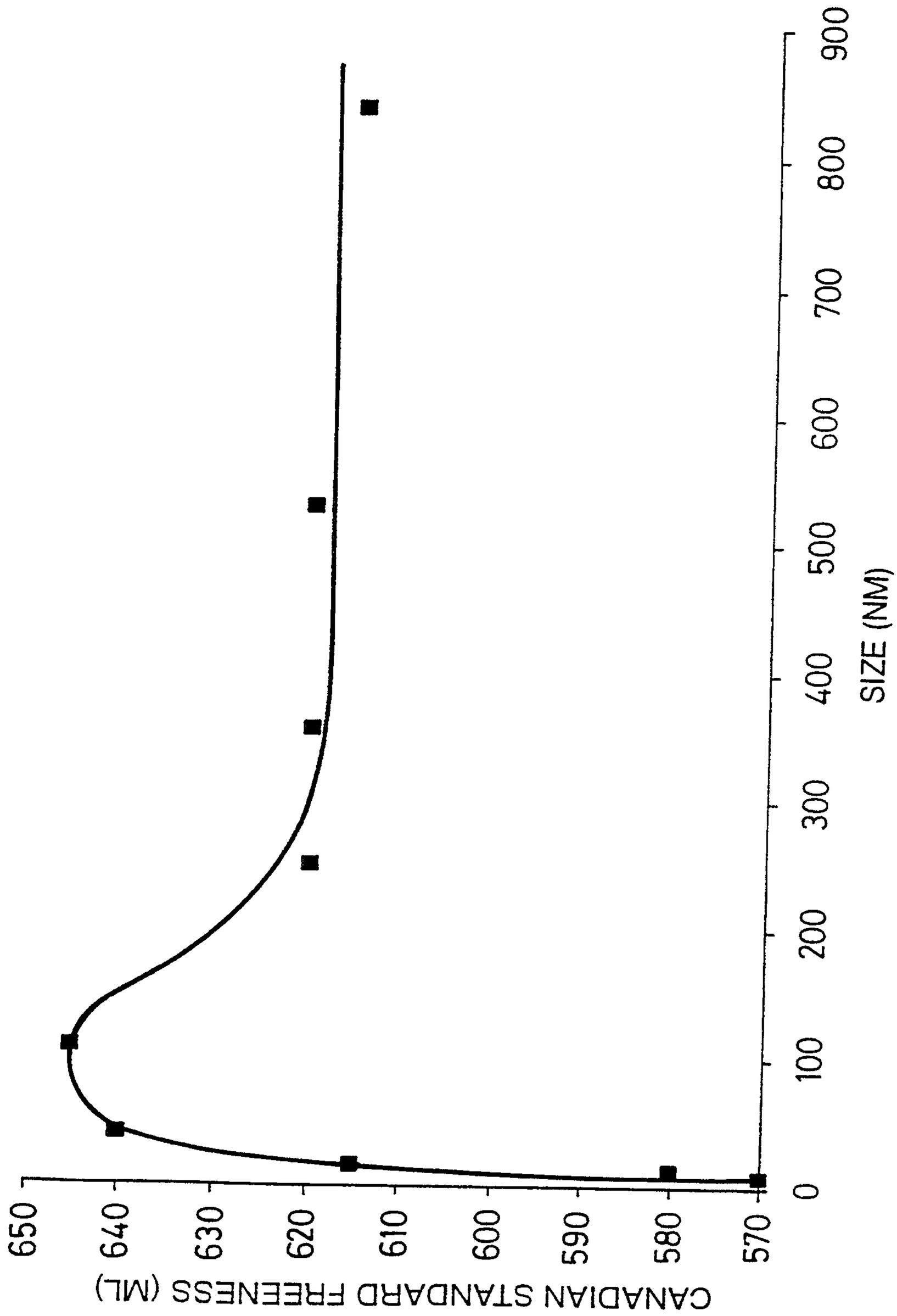

CANADIAN STANDARD FREENESS (ML)
650
640
630
620
610
600
590
580
570
0
100
200
300
400
500
600
700
800
900
SIZE (NM)

FIG. 4

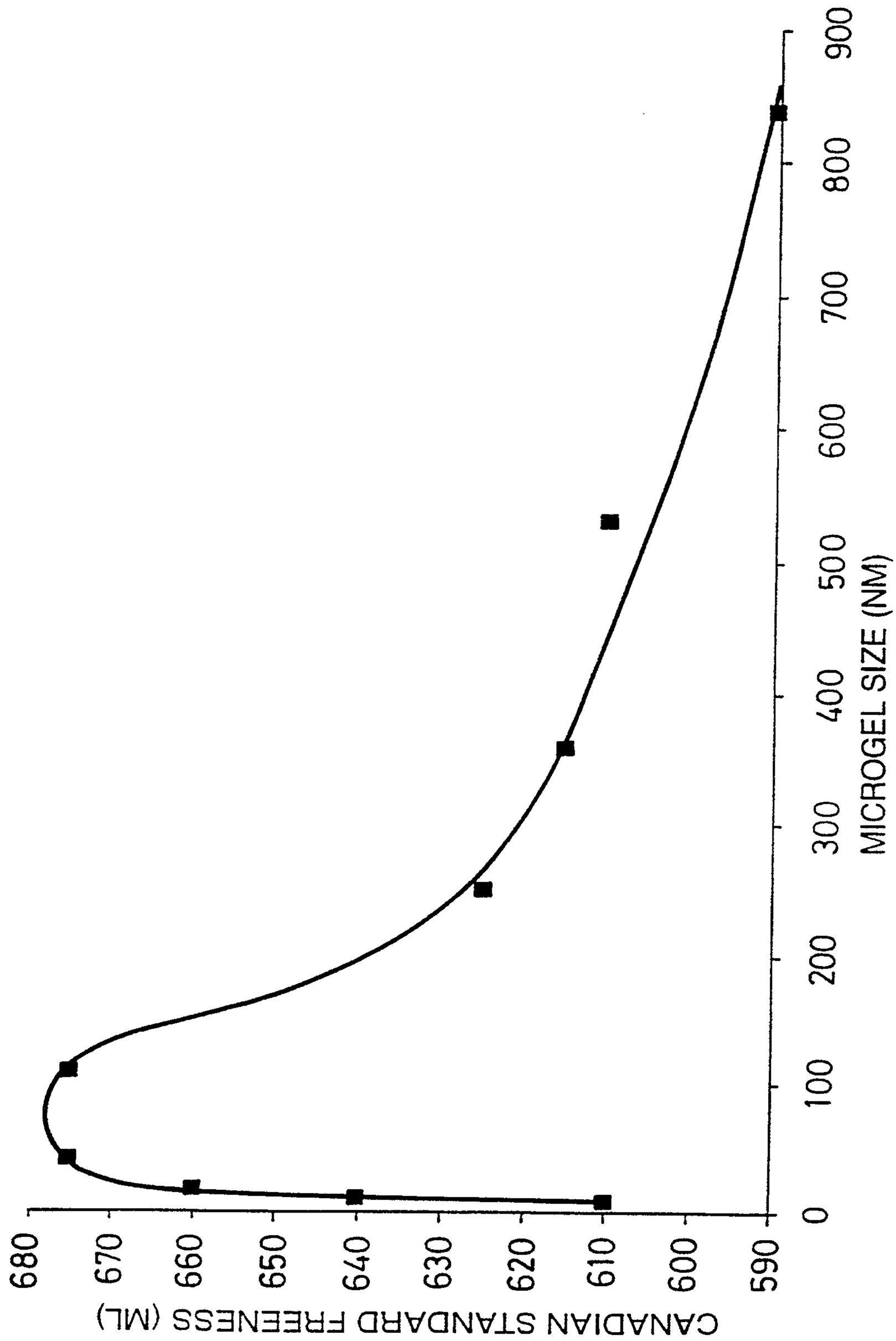
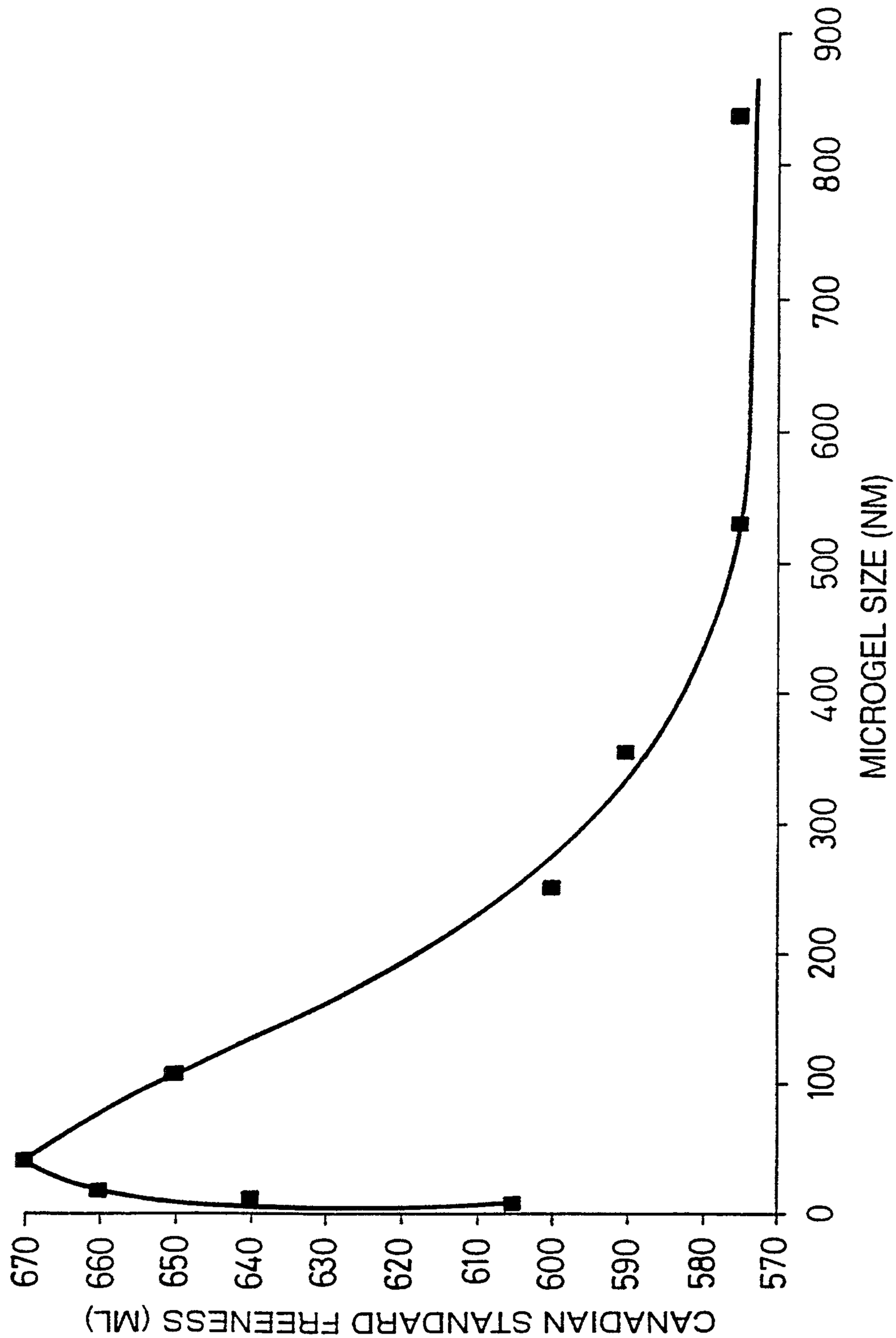
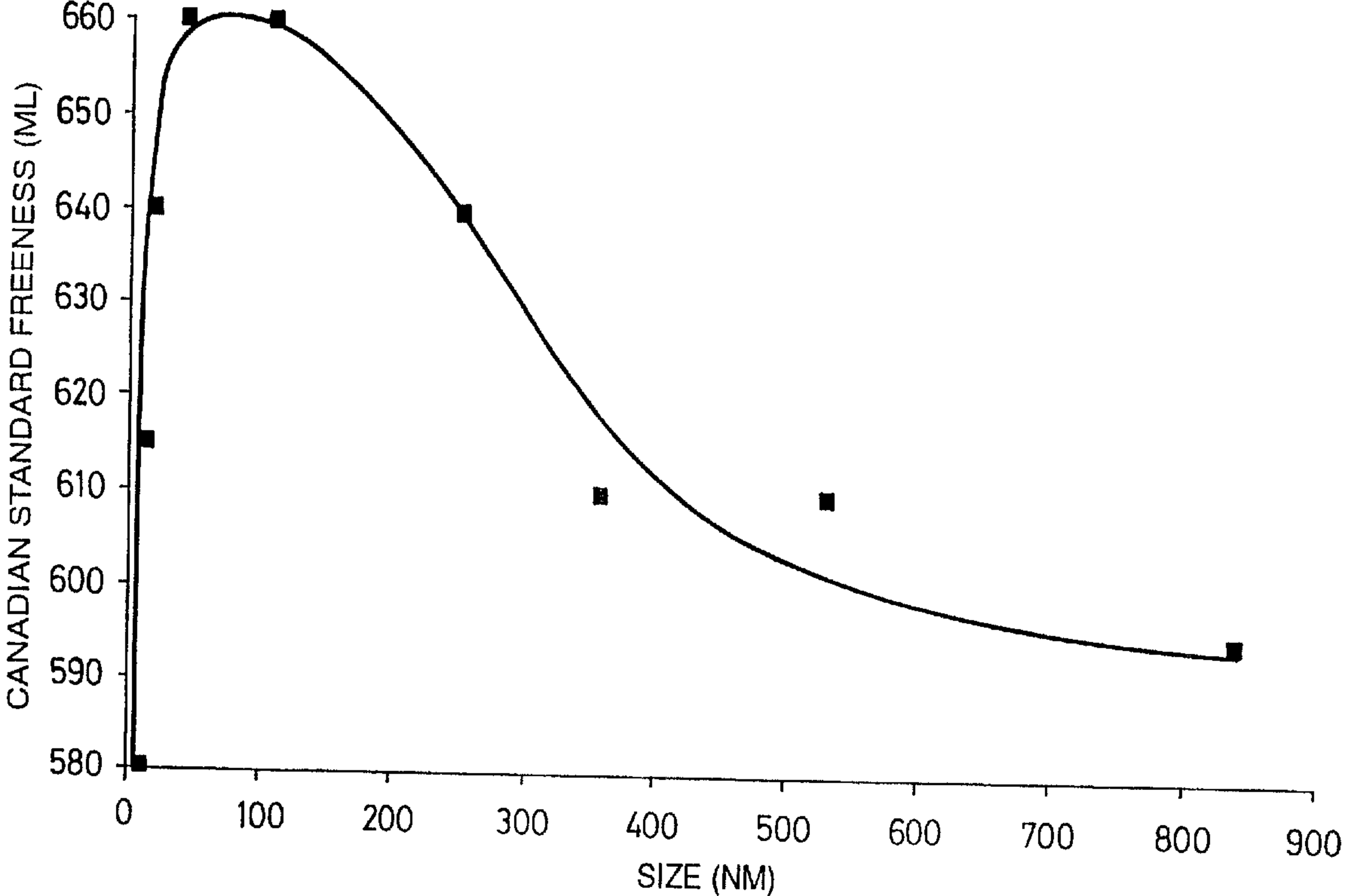

CANADIAN STANDARD FREENESS (ML)
680
670
660
650
640
630
620
610
600
590
0
100
200
300
400
500
600
700
800
900
MICROGEL SIZE (NM)

FIG. 5


CANADIAN STANDARD FREENESS (ML)
670
660
650
640
630
620
610
600
590
580
570
MICROGEL SIZE (NM)
0
100
200
300
400
500
600
700
800
900


CANADIAN STANDARD FREENESS (ML)
660
650
640
630
620
610
600
590
580
0
100
200
300
400
500
600
700
800
900
SIZE (NM)