Net Density of Ramie Cellulose

By

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Abstract

A method of measuring the densities of fibrous, powdery and porous substances, which are liable to occlude gases and water, is described. With this method the density of retted ramie-fibre is observed to be 1.622, and those of purified and mercerized ramie cellulose are observed to be 1.614 and 1.610 respectively. These are the greatest values observed hitherto.

In a paper[1] recently published, one of the writers and N. Matsumoto suggested that the net density of cellulose was probably somewhat higher than the values hitherto observed. Since then, the writers have attempted to get more accurate values of the densities of retted ramie fibre, purified and mercerized ramie cellulose. The method and the results of the measurements are described below.

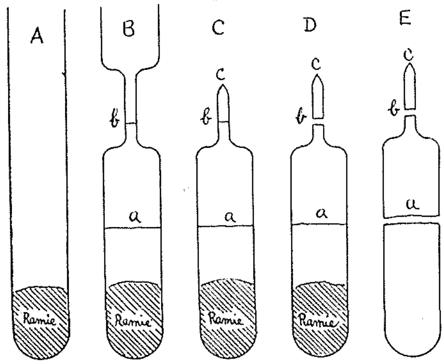
The point, to which most attention must be paid in this kind of measurement, is how to take off the gas and the water which are occluded in the specimen. This was simply done by heating and evacuating properly the glass tube containing the specimen. The procedure of the experiment is illustrated in Fig. 1.

A certain quantity of the specimen, which had been kept in a desiccator, was weighed with a balance, and it was put into a glass tube which had been sealed at one end, as is shown by A in Fig. 1. A part of the tube was necked with a burner several centimeters from its sealed end as is shown by B in the same figure. Sufficient care was taken, of course in this case, not to heat the specimen contained in the sealed end. The tube was scraped with a file at the parts marked *a* and *b* in B, Fig. 1, so as to be easily broken after-

1. U. Yoshida and N. Matsumoto, These Memoirs, **14**, 115 (1931)

wards. Then the tube was connected to an oil rotary pump which was capable of evacuating down to a pressure of about 0.01 mm. of mercury. When the tube was being evacuated, the tube was kept at a proper temperature by being placed in a water or an oil bath. When the evacuation was ended the tube was sealed at its neck as shown in C, Fig. 1. The tube thus sealed was weighed, and then its volume was measured by immersing it in water contained in a measuring cylinder. The volume of the sealed tube thus observed served for the reduction of weighing in vacuo; and the values of those treated in the present experiment were from 7 to 13 c.c. Distilled water was then introduced into the tube by breaking the neck of the tube at *b* in distilled water in the way shown by D in Fig. 1. In this case some small bubbles were usually seen in the tube even when the tube was evacuated thoroughly. These bubbles were not due to imperfect evacuation, but they were confirmed to be caused by the evolution of air which had been absorbed by the water. To avoid as far as possible the formation of the air bubbles, the distilled water was first boiled, cooled as quickly as possible by dipping the vessel containing the boiled water in running water, and then the water thus cooled was introduced into the evacuated glass tube containing the specimen by breaking the neck of the glass tube at the point *b* in the cooled water. Even with this procedure some bubbles of much smaller size were seen to be still formed in the tube. But these small bubbles were observed to disappear entirely on merely leaving the tube in the cooled water for more than about five hours in the present case. This is probably due to the reabsorption of the evolved air into the water. This precaution to eliminate the presence of air bubbles is very important, and it was always taken when accurate determination of the density was wanted.

Fig. 1



Next the weight of the specimen in distilled water was measured. After the weight in distilled water of the glass tube containing the specimen, and the broken neck, both of which were perfectly filled with water, had been measured in the usual way, the glass tube was broken along the filed line *a*, and the specimen was taken out of the tube. Then the weight in distilled water of all the parts of the broken glass tube, as shown by E in Fig. 1, was measured in the same way, and the weight of the specimen only in distilled water was obtained immediately.

Finally after all the parts of the broken glass tube had been freed from water and well dried, their weight in air was measured. From the weight of the glass tube only and that of the sealed glass tube containing the specimen which was well evacuated, we can obtain immediately the net weight of the specimen. From this net weight of the specimen and its weight in distilled water, the net density of the specimen was calculated.

In the procedure above stated, the reduction of weighings in vacuo and the correction due to the change of the density of water with temperature were, of course, always made.

As preliminary experiments, the writers measured the densities of retted ramie fibre, purified and mercerized ramie cellulose, evacuated for various duration of time by being heated to different temperatures in the bath. The results of the experiments are shown in Figs. 2 and 3. In the case of Fig. 2 the time of evacuation was kept constant at 7 hours, and the temperature of the bath changed from the room temperature to 160°C. This temperature of the bath being taken as abscissa, the densities of retted ramie fibre and cellulose are represented as ordinate in the upper half of Fig. 2; and the reduction of weight of the specimen by evacuation, which is represented in percentage with reference to the original weight of the unevacuated specimen, is taken as ordinate in the lower half of the same figure.

Fig. 2

△ for retted ramie fibre,
× for purified cellulose,
○ for mercerized cellulose

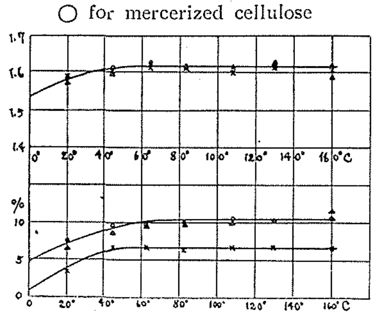
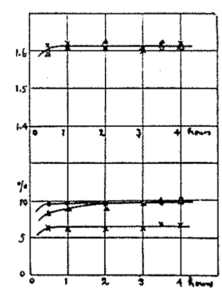


Fig. 3

△ for retted ramie fibre
× for purified cellulose
○ for mercerized cellulose



In the case of Fig. 3 the temperature of the heating bath was kept constant at 70°C, and the time of evacuation changed from 30 minutes to 4 hours. The time of evacuation is taken as abscissa in this case, and the ordinates in the upper and the lower halves have the same meaning respectively as in Fig. 2 From the curves in Figs. 2 and 3, we know that when the specimen is heated at 70°C, the density and the reduction in weight remain unchanged for evacuations of longer than about two hours, and that when the time of evacuation is seven hours, the density and the reduction in weight reach their maximum values and remain constant for heatings higher than about 50°C, so far as the present experiment is concerned. The fact that the density and the reduction in weight attain their maximum values at a certain stage means that at least nearly all the gas and water occluded in the specimen are driven out at this stage. Thus a reliable value for the density will be obtained under the conditions which provide such maximum values of density and reduction in weight; and the value of the density of retted ramie fibre and ramie cellulose, which is taken to be most reliable as will be stated later, was obtained under such conditions.

Here it must be noted that when the specimen is heated to a temperature higher than about 130°C a slight carbonization begins to occur. Thus the heating of the specimen to a temperature higher than this must be avoided when an accurate density is required.

As the experiments shown in the curves in Figs. 2 and 3 were preliminary, the writers did not use much of the specimen, the quantity being usually several decigrams in each experiment.

Table I

Net Density

Retted ramie fibre	Purified ramie cellulose	Mercerized ramie cellulose	Remark
			Evacuated for
1.620	1.612	1.608	7 hours at 77°C
1.621	1.613	1.611	3.5 hours at 75°C
1.624	1.617	1.612	4 hours at 70°C
1.622	1.614	1.610	Mean density

Here it must be remarked that the present experiment was performed under the assumption that the net density of cellulose does not suffer any appreciable change by its swelling in water. If there is any suspicion on this point, it will be safer to measure again the density of cellulose by dipping it into some suitable liquid other than water.

By taking the various precautions stated before, the measurements of the most reliable densities of retted ramie fibre, purified and mercerized ramie cellulose were performed and the results are tabulated in Table I. The quantity of the specimen used in this case was from 0.7 gms. to 1.7 gms.; and the probable error of the measurements was about $\pm$ 0.3 per cent. The density of the retted ramie fibre is 1.622, and it is somewhat larger than those of the others. Though the density of the purified ramie cellulose is a little larger in the table than that of the mercerized, the difference is smaller than the limit of experimental error, and consequently they may be looked upon as nearly the same.

So far as the writers are aware, the values of the densities of retted ramie fibre, purified and mercerized ramie cellulose obtained by them are larger than those observed hitherto for cellulose. For example, O. L. Sponsler[1] took 1.57, R. O. Herzog[2] 1.52 and K. R. Andress[3] 1.59 as the density of pure cellulose.

If some small cavities which do not permit the intrusion of water existed in the tissue of the fibre, then the density of the specimen measured would be smaller than the net value even with the method employed by the writers. The presence of such small cavities was examined for microscopically with a specimen soaked with water, which had been well degassed previously by the method mentioned before. But no trace of the presence of such small cavities and of small bubbles on the surface of the specimens could be detected. This result seems to deny the possibility of much greater values for the densities of retted ramie fibre, purified and mercerized ramie cellulose, than those observed by the writers.

It has already been stated that the weight of the specimen decreases with evacuation in parallel with the increase in its density. This seems to be mainly due to the expulsion of water occluded

1. The Journal of General Physiology, **7**, 677 (1926)
2. The Journal of Physical Chemistry, **30**, 457 (1926)
3. Zs. f. phys. Chem., **136**, 279 (1928)

Table II

Retted			Purified			Mercerized			
Density of evacuated ramie	Reduction of weight by evacuation in %	Density of unevacuated ramie (calc.)	Density of evacuated ramie	Reduction of weight by evacuation in %	Density of unevacuated ramie (calc.)	Density of evacuated ramie	Reduction of weight by evacuation in %	Density of unevacuated ramie (calc.)	
1.618	9.85	1.524	1.606	6.5	1.545	1.611	9.84	1.520	
1.612	10.06	1.517	1.594	6.64	1.535	1.606	10.41	1.512	
1.626	10.15	1.530	1.610	6.62	1.546	1.614	10.25	1.518	
1.616	10.00	1.521	1.606	6.01	1.548	1.617	9.88	1.523	
1.608	8.80	1.526	1.614	6.25	1.553	1.610	9.83	1.518	
1.622	8.83	1.537	1.608	6.12	1.550	1.607	9.04	1.523	
1.592	8.26	1.516	1.613	6.28	1.553	1.603	9.46	1.516	
1.540	3.67	1.511	1.587	3.34	1.556	1.558	5.59	1.512	
1.533	3.74	1.503	1.573	3.42	1.544	1.553	5.54	1.506	
		1.521			1.548			1.516	Mean value
		1.528			1.541			1.511	observed by using freezing mixture
		1.47			1.544			1.507	Direct observ.

in the specimen, because the colour of the electric discharge through a Geissler tube, connected in parallel with the glass tube containing the specimen, is the same as that peculiar to hydrogen gas. Thus by assuming that the reduction in weight by evacuation is entirely due to the extraction of liquid water adhering to the specimen, the writers calculated the densities of the unevacuated specimens, and they are given in the third, sixth and ninth columns in Table II respectively for the retted ramie fibre, and purified and mercerized ramie cellulose. The values thus calculated are nearly the same respectively for each one of the three kinds of the specimens. The mean values for the three different kinds of specimens are given in the third horizontal row from the bottom in Table II. The values given in the second horizontal row from the bottom are obtained by evacuating the specimens for about 30 minutes by cooling them in a freezing mixture, so as to prevent the extraction of liquid water from the specimens as far as possible. The agreement between the values given in the third and the second horizontal rows from the bottom of the table seems to be almost satisfactory for the three different kinds of specimens respectively. This seems to justify our previous assumption that the reduction of weight of the specimen by evacuation is mainly due to the expulsion of liquid water adhering to the specimen. The values of the densities given in the horizontal row at the bottom of the table are those measured in the usual way without any evacuation. The values for the purified and mercerized cellulose are in fair agreement with those obtained with evacuation by cooling the specimens with freezing mixture. However the value for the retted ramie fibre is much smaller than that obtained with evacuation by cooling with freezing mixture. This is caused by the presence of very small air bubbles adhering tightly to the ramie fibre when it is immersed in water. Thus the value of the density, 1.47, for the retted ramie fibre is entirely erroneous.

It seems to be not unprofitable to mention that the reduction in weight by evacuation is nearly the same for the retted ramie fibre and the mercerized ramie cellulose; and that that for the purified ramie cellulose is much smaller than those for the former two. The value for the former two is 10% and that for the latter is 6.5% of the original weight when the specimens are thoroughly evacuated. This shows that the purified ramie cellulose is less hygroscopic than the other two.

Table III

Reduction of weight in % refering to the original weight

	Retted ramie fibre	Purified ramie cellulose	Mercerized ramie cellulose
Dried in desiccator	1.81	1.36	1.84
Evacuated thoroughly	9.87	6.88	10.76

After all the experiments described above had been finished, the writers found that the exsiccant in the desiccator which had been used to dry the specimens had become very dull, and that the weight of the specimen was the same regardless of whether it was kept in the desiccator or left in free air. Thus the old exsiccant was replaced by a new one, and the specimens were kept in the desiccator filled with the new exsiccant for several days. During this time the specimens were weighed occasionally, and their weights were seen to diminish gradually till they reached some stationary value after about two days. The reduction in weight at this stationary state, which is expressed in percentage with reference to the original weight, is given in the second horizontal row of Table III. The reduction in weight is nearly the same for the retted ramie fibre and the mercerized ramie cellulose, and that for the purified cellulose is smaller than that for the former two, in accordance with the fact observed before. The reduction in weight of the specimens when they are thoroughly evacuated is given in the horizontal row at the bottom of the same table.

Here it must be noted that the method described above for measuring the density accurately, can be well applied to any substances, such as powdery, fibrous or porous substances, which are liable to occlude gases and water.

In conclusion, the writers wish to express their sincere thanks to Prof. G. Kita of the department of industrial chemistry for his kindness in giving various suggestions and also in furnishing all the test materials to the writers. They wish also to express their hearty thanks to Prof. K. Koriba of the botanical department for the interest he has taken in the research, and also to Mr. H. Komuro for his kindness in examining the specimens with the microscope.