CELLULOSE INDUSTRY
THE JOURNAL OF THE CELLULOSE INSTITUTE, TOKYO, JAPAN
VOL. 10 March, 1934, No. 5

ABSTRACTS FROM THE TRANSACTIONS

THE SORPTION OF WATER VAPOUR BY ACETYL-CELLULOSE.

By Ryo SHINODA.

Introduction.

The sorption of water vapour by acetyl-cellulose is a matter of great practical as well as theoretical importance, because the acetyl-cellulose is widely used as a material for dope, artificial silk, plastic mass etc., one of the properties of which must be water-proof. There have been found many investigations as to the sorption of water vapour by cellulose itself since it was emphasized by the great pioneer of cellulose investigator, Cross and Bevan. Literatures relating to that of acetyl cellulose, however, are very scanty; especially regarding the relation between the sorption of water vapour and the number of acetyl groupe of acetyl-cellulose there has appeared no concrete investigation. The present author therefore has carried out some experiments on this line for the purposes of revealing abviously that relation, and, moreover, the sorption velocity, the sorption isotherm of acetyl-cellulose etc., the work done being a contribution to the following problems:

1. Sorption capacity of water vapour and its velocity of acetyl-cellulose.
2. Relation between sorption capacity of water vapour and acetyl group in acetyl-cellulose.
3. Relation of Sorption capacity of water vapour by acetyl-cellulose to temperature and relative humidity.
4. Sorption capacity of water vapour by other cellulose derivatives: such as benzyl-cellulose, ethyl-cellulose and acetyl-mannan.

Experimental.

Materials: The samples used in these determinations were primary and secondary acetyl-celluloses, which were prepared in my laboratory by the method previously reported by both K. Atsuki and R. Shinoda in "Report of the aeronautical research institute, Tokyo Imperial Univercity, 1928, **3**, No. 35; and other samples were three kinds of secondary acetyl-cellulose obtainanle from Eastman Kodak Company in U. S. A., Co. Francaise de produits chimiques et Matieres Colorantes de Clain de Rhone in France and Germany as raw material for dope. The properties of these samples are listed in the Table II.

Method: Heated for about 5 hrs at 60°C under vacuum, the samples were finally dried in a desiccater containing P_2O_5 until a constant weight was attained. About 1—4g. of the samples thus

treated were put into small glass vessels particularly made from thin glass, being 40 mm in diameter and 40 mm in height. These vessels containing samples were placed one by one in second glass vessels, pressure and humidity in which were able to be regulated by means of the manometer attached to them and by varying the concentration of sulphuric acid contained in them. The second vessels were placed in an air thermostatt to give a desired temperature to them. All the samples were stirred every 0.50 hrs with a small agitator made of platinum wire to make the sorption of water vapour uniform. After a desired time, the first vessels were covered with lids and weighed, the increased weights being calculated as the percentage on the dried sample, called them sorption capacity.

Results and discussion.

A) Sorption capacity of water vapour and its velocity of acetyl-cellulose.

The results obtained from the various kinds of primary and secondary acetyl-cellulose at 20°C and 100% relative humidity are listed in the following Table I.

Table I.
Sorption capacity (% on the dried Sample).

Kinds of Sample.	1 h.	2 hs	4 hs	6 hs	8 hs	32 hs	88 hs	Mas sorp. cap.
I-acetyl-cellulose from tissue paper	0.37	0.87	1.64	2.39	2.91	5.27	7.11	7.52
I-acetyl-cellulose from hydro-cellulose	0.43	1.09	2.00	2.74	3.39	5.89	7.14	7.95
I-Acetyl-cellulose from oxycellulose	0.47	0.89	1.85	2.64	3.26	5.97	7.51	8.0
I-Acetyl-cellulose from Hydrated cellulose	0.47	1.01	2.09	2.92	3.52	7.12	9.90	9.90
I-Acetyl-cellulose from wood-cellulose	0.45	0.92	1.45	2.06	2.62	5.16	6.76	6.92
II-Acetyl-cellulose I	1.35	2.93	4.66	6.14	7.13	10.03	13.50	13.55
II-Acetyl-cellulose II	1.06	2.14	4.04	5.10	6.80	11.43	14.10	14.30
II-Acetyl-cellulose made in Eastman Kodak Co.	0.91	1.93	3.56	4.54	5.33	8.76	11.75	11.36
II-Acetyl-cellulose made in Germany	1.25	2.55	4.04	5.49	6.53	11.12	14.44	14.44
II-Acetyl-cellulose made in France	1.26	2.73	3.30	3.71	5.75	7.79	9.92	12.78

Remarks: Samples are 20—25 mesh in size.

Fig. 1.

These data obtained are plotted in the Figure I. It will be seen from the above results that the I-acetyl-cellulose has extremely smaller sorption capacity of water vapor than secondary has; this fact could be considered to depend mainly upon the number of hydroxyl group contained in acetyl-cellulose. The former is less in number of hydroxyl group than the latter. Not only depends the sorption capacity upon the hydroxyl group, but also upon the degree of degradation and the physical form of acetyl-cellulose. It is able to see this phenomenon clearly from the above results.

The sorption velocity of acetyl-celluloses,

both primary and secondary acetyl-cellulose, is very rapid until 80—90% of sorption capacity is attained and then extremely slow, as is evident in the Figure I. In other words, there appears to be two stages or aspects of the sorption of water vapour by acetyl-cellulose. One probably consists principally in attachment of hydroxyl group to acetyl-cellulose, it might be called "Chemosorption", the other seems to depend mainly upon "Capillary condensation". The sorption velocity of the first stage is given by the following equation.

$$\frac{dS}{dt} = K(S_m - S_t), \quad \text{i.e.} \quad K = \frac{1}{t} \ln \frac{S_m}{S_m - S_t}$$

in which S_m is the maximum sorption capacity, S_t is the sorption capacity at a given time, t is the time during sorption, and K is a constant. For the second stage the following equation seems to be applicable.

$$\frac{dS}{dt} = \frac{K}{R}, \quad R = at \quad \text{i.e.} \quad S - a \log t = K'$$

where R is resistance to enter into capillary of samples, t is time during sorption, K and K' are constants, and S is the sorption capacity.

B) Relation between sorption capacity of water vapour and acetyl group in acetyl-cellulose.

The results obtained for the determination of the relation between the sorption capacity of water vapour and the acetyl group in acetyl-cellulose are tabulated in the following table II.

Table II.

Samples	acetyl group %	Cu. No.	sorption capacity	acetyl group + sorption capacity
I-acetyl-cellulose from tissue paperI	61.81	1.91	7.55	69.36
ditto.....II	60.54	1.75	7.88	68.42
ditto.....III	62.20	1.79	7.32	69.52
I-acetyl-cellulose from wood-cellulose	62.76	2.53	7.88	70.64
I-acetyl-cellulose from cellulose Hydrate.....I	61.28	1.86	8.23	69.51
ditto.....II	57.35	3.78	9.48	66.83
I-acetyl-cellulose from hydrocelluloseI	69.53	2.43	7.61	77.60
ditto.....II	67.06	3.45	6.90	73.96
ditto.....III	72.41	3.28	6.83	79.24
I-acetyl-cellulose from oxycelluloseI	60.89	2.36	7.55	68.44
ditto.....II	61.49	2.36	8.70	70.19
ditto.....III	61.43	6.62	7.04	68.43
ditto.....IV	61.04	6.99	8.83	69.87
II-acetyl-cellulose.....I	56.77	2.15	12.55	69.32
ditto.....II	56.45	3.28	13.65	70.10
ditto.....III	55.63	3.94	13.51	69.14
ditto.....IV	57.56	3.62	12.41	69.91
ditto.....V	54.50	5.44	15.20	69.70
II-acetyl-cellulose made in France	52.49	2.95	12.78	65.27
II-acetyl-cellulose made in Germany	53.58	2.96	14.44	68.02
II-acetyl-cellulose made in U. S. A.	57.55	2.62	11.36	68.91

From the above results it will be seen that there is intimate relation between the sorption capacity of water vapour and the acetyl group of acetyl-cellulose, i.e.: The sums of the sorption capacity of water vapour and the acetyl group of acetyl-celluloses are almost equal, except the case of considerable degradation of acetyl-cellulose. The mean values of "Number of acetyl group + the sorption capacity" for primary and secondary acetyl-cellulose are 69.47 and 69.37 respectively.

If the sorption capacity of water vapour were merely affected by hydroxyl group of acetyl-cellulose, the theoretical tri-acetyl-cellulose should take up no more water vapour, namely the sorption capacity might be zero. While the results obtained showed that even primary acetyl-cellulose having approximately theoretical tri-acetyl group absorbed about 7.17% ($69.42 - 62.25 = 7.17$) of water vapour. It is natural to consider that this number is the sorption capacity mainly caused by the rate of degradation and the physical form of primary acetyl-cellulose and it might be called proper sorption capacity. In the case of secondary acetyl-cellulose, as to the proper sorption capacity, we could consider the same meaning as that of primary acetyl-cellulose, viz. 7.12 ($67.39 - 62.25 = 7.12$) is the proper sorption capacity of secondary acetyl-cellulose.

The total sorption capacity of secondary acetyl-cellulose is generally more than 10%. Consequently, it is proper to regard that the number to be obtained by subtracting the proper sorption capacity from the total sorption capacity should be the sorption capacity depending principally upon hydroxyl group of acetyl-cellulose. For instance: In the case that the total sorption capacity is 13.65% (refer to the Table II) $13.65 - 7.12 = 6.53$ is caused by hydroxyl group. If the above assumption is correct, the sum of number of acetyl group and 6.53 should be totald to the theoretical number of acetyl group 62.25. As the acetyl group of this sample is 56.45% (refer to the Table II), the sum of that number and 6.53 will became $56.45 + 6.53 = 62.98$, nearly the theoretical number; therefore the above assumption is verified to be correct. Furthermore, the author has attempted to formulify the relation between sorption capacity and acetyl group. The sorption capacity increases linearly with the decrease of acetyl group, as shown in Fig. 2. Consequently, the relation between the both can be expressed by the following equation.

$$x = my + K$$

Where x is the total sorption capacity of water vapour, y is the number of difference between theoretical and the measured acetyl group, m is a constant depending upon temperature and humidity, and k is the so called proper sorption capacity.

The acetyl-cellulose acetylated higher than tri cellulose has merely the so called proper sorption capacity. With regards to range of application of this equation to the acetyl-cellulose having extremely low acetyl group, it is necessary to carry out somewhat further experiment.

The author has attempted to apply this

Fig. 2.

equation determined for acetyl-cellulose to the relation between the sorption capacity of water vapour and the nitrogen content of nitrocellulose and has found it is so adaptable to the case of nitrocellulose.

C) Relation of the sorption capacity of water vapour by acetyl-cellulose to temperature and relative humidity.

In order to observe effects of temperature and relative humidity on the sorption capacity of water vapour by acetyl-cellulose, the author has carried out some experiments at 13°C, 18°C, 20°C and 35°C respectively in each case of relative humidity 100% and 45%, dealing with primary and secondary acetyl-celluloses. The following Table III gives the results obtained.

Table III.									
In the case of 100% relative humidity					In the case of 45% relative humidity				
	Time measured \ Temp.	13°C	18°C	35°C		Time measured \ Temp.	13°C	20°C	35°C
I-acetyl-cellulose	2	0.78	0.88	—	2	0.21	0.21	0.05	
	4	1.03	1.19	—	6	0.34	0.33	0.12	
	10	2.01	1.84	1.51	10	0.54	0.45	0.41	
	20	3.61	3.40	2.38	20	0.98	0.81	0.67	
	40	5.83	5.10	3.43	50	1.82	1.63	1.29	
	80	7.02	6.55	5.20	100	2.40	2.12	1.73	
	120	7.50	6.93	5.90	Max. sorp. cap.	2.52	2.13	1.81	
	Max. sorp. cap.	7.71	7.56	6.12					
II-acetyl-cellulose	2	2.01	2.20	—	2	1.3	—	—	
	4	3.60	3.10	—	6	2.5	1.4	1.0	
	10	5.20	4.30	—	10	4.2	2.4	1.8	
	20	8.02	7.61	6.20	20	6.5	9.8	2.75	
	40	10.96	9.03	9.10	50	8.4	4.6	3.80	
	80	12.50	13.85	10.50	100	10.2	5.4	4.20	
	120	13.50	13.65	11.40	Max. sorp. cap.	10.61	5.8	4.42	
	Max. sorp. cap.	13.99	13.65	12.10					

Remarks: Acetyl group of primary and secondary acetyl-cellulose are 61.81%, 56.45% respectively.

It will be seen from the above results that the sorption capacity of water vapour by acetyl-cellulose decreases with the rise of temperature, because it is exothermic reaction, the heat of sorption of which can be calculated by the equation $Q = \frac{R.T_1.T_2}{M(T_2 - T_1)} (\log P_2 - \log P_1)$ (Sheppard and Newsome, *J. Phys. Chem.*, 1932, 930). While, according to the equation $\left(\frac{x}{m}\right) = P$, the amount of water vapour absorbed by acetyl-cellulose should increase with increase of pressure, thereby from this view, the sorption capacity must increase with the rise of temperature. The experiment results, however, were entirely contrary. This fact, therefore, indicates that the effect of temperature on the sorption of water vapour is larger than that of pressure. As to the applicability of the equation obtained for the relation between the sorption capacity of water vapour and acetyl group i.e. $x = my + K$, the author could not determine whether that equation is applicable to these cases of varying the temperature or not, because of shortage of the data

obtained, but it was decidedly verified by utilizing the data obtained by will that the equation is applicable to the case of nitrocellulose at any temperature, as shown in the following Table IV.

Table IV.

N. content %	at 25°C			at 15°C			at 5°C		
	obs. value	calc. value	diff.	obs. value	calc. value	diff.	obs. value	calc. value	diff.
13.20	1.42	1.46	0.04	2.75	2.63	-0.12	3.00	2.90	-0.10
12.68	1.95	1.95	0.00	3.40	3.47	-0.07	3.50	3.75	-0.25
12.06	2.43	2.51	-0.08	4.30	4.30	0.00	4.61	4.61	0.00
11.00	3.55	3.59	-0.04	5.52	5.75	-0.23	6.01	6.05	-0.04
9.87	4.74	4.53	-0.21	7.35	7.25	-0.10	8.10	7.60	-0.50

Remarks:

$$x = my + K$$

$$m = 0.92$$

$$m = 1.35$$

$$m = 1.37$$

$$K = 0.60$$

$$K = 1.50$$

$$K = 1.75$$

in the case of 25°C

in the case of 15°C

in the case of 5°C

The results obtained regarding to the relation between sorption capacity and relative humidity are as follows.

Table V.

Samples	Relative humidity %		
	45%	75%	100%
I-acetyl-cellulose	2.13	4.25	7.55
II-acetyl-cellulose	4.82	9.03	13.56

Fig. 3.

The graphical expression of the above results is as following Figure 3.

From the above results it will be noticed that the sorption capacity increases with increase of relative humidity, that of secondary acetyl-cellulose being larger than that of primary. The sorption isotherm of acetyl-cellulose seems to follow to the isotherm equation, $y = \frac{x}{a - bx - cx^2}$,

developed by S. Oguri from the Langmuir's equation $x = \frac{abp}{1 + ap}$ (J. Am. Chem. S., 1918, 40, 1388).

D) The Sorption capacity of water vapour by other cellulose derivatives: such as benzyl-cellulose, ethyl-cellulose and acetyl mannan.

In order to compare the sorption capacity of water vapour by these cellulose derivatives with each other; such as acetyl-, ethyl-, benzyl-cellulose and acetyl-mannan, the author has carried out some experiments. The results obtained are in the following Table VI and the plotted Figures 4 and 5.

Table VI.

Sample	Relative humidity %	Sorption capacity				
		3 hrs	5 hrs	20 hrs	75 hrs	Max. sorp. cap.
Acetyl-cellulose	100	4.017	6.803	11.860	15.858	16.458
Acetyl-mannan		3.413	5.391	10.187	12.456	12.712
Benzyl-cellulose		0.711	0.994	1.506	2.108	2.150
Ethyl-cellulose		2.744	4.387	7.622	10.845	10.815
Acetyl-cellulose	75	3.199	4.758	6.367	6.504	7.302
Acetyl-mannan		3.036	3.731	4.289	4.574	4.883
Benzyl-mannan		0.460	0.567	0.603	0.532	0.582
Acetyl-mannan		1.781	2.441	3.718	3.915	4.213
Acetyl-cellulose	40	1.562	2.126	2.616	3.107	3.823
Acetyl-mannan		1.216	1.537	1.800	2.097	2.437
Benzyl-cellulose		0.232	0.258	0.271	0.354	0.423
Ethyl-cellulose		0.808	1.003	1.111	1.193	1.592

Fig. 4.

Fig. 5.

The sorption capacity of water vapour is the largest in acetyl-cellulose. It becomes smaller in acetyl-mannan, ethyl-cellulose and benzyl-cellulose in these turn, and benzyl-cellulose has the smallest sorption capacity. The sorption velocity of these substances seems to follow to the equation obtained for acetyl-cellulose in the previous chapter. For the sorption isotherm the equation previously described can be adapted for acetyl-mannan and ethyl-cellulose, while for benzyl-cellulose it seems not to be applicable.

Summary.

The conclusions drawn from the results obtained are summarized as follows:

- (1) The sorption capacity of water vapour by primary cellulose is extremely smaller than that of secondary. It probably depends upon the differences in number hydroxyl group, the rate of degradation and the physical contraction between the both.

The sorption velocity of water vapour by acetyl-cellulose is generally larger in secondary acetyl-cellulose than in primary. There appears to be two stages. One seems to follow to the equation $\frac{dS}{dt} = K(S_m - S_t)$, i.e. $K = \frac{1}{t} \ln \left(\frac{S_m}{S_m - S_t} \right)$, where K is the sorption velocity constant, t is a time during sorption, S_m is the maximum sorption capacity and S_t is the sorption capacity at a given time, the other being given by the equation $S - a \log t = K$, where K is sorptions velocity constant, S is the sorption capacity, t is a time during sorption and a is a costant depending on the kind of sample.

(2) The relation between the sorption capacity of water vapour and the number of acetyl group of acetyl-cellulose seems to be expressed by the following equation

$$x = my + K$$

where x is the sorption capacity, y is the difference between the theoretical acetyl group of tri-acetate and the measured acetyl group, K and m are constants depending upon temperature and humidity. This equation appears to be aplicable to the case of the relation between sorption capacity of water vapour and nitrogen content of nitro-cellulose.

(3) The sorption capacity of water vapour decreases with rise of temperature. The effect of temperature on the sorption capacity is larger than that of water vapour pressure. The sorption isotherm is subjected by the equation $\frac{x}{a + bx - cx^2} = y$, developed by S. Oguri from the Langmuir's equation where x is relative humidity, a , b , c , are constants and y is the sorption capacity.

(4) The sorption capacity of water vapour by cellulose derivatives is the largest in acetyl-cellulose: Acetyl-mannan, ethyl-cellulose and benzyl-cellulose diminish their capacity in order described. Benzyl-cellulose has the smallest capacity. For the sorption velocity and the sorption isotherm of these samples are also applicable the same equation as that preciously obtained for acetyl-cellulose. But benzyl-cellulose alone does not follow to the equation of sorption isotherm.

In conclusion the author wishes to express his gratitude to Prof. K. Atsuki for his invaluable suggestion throughout the course of the study. He also thanks the authorities in the Military Scientific Institute for giving a permit to publish this paper.