

Softener Absorption by Regenerated Cellulose

ROMAN MYKOLAJEWYCZ*, ERIC WELLISCH, RICHARD N. LEWIS, and ORVILLE J. SWEETING

Film Division, Olin Mathieson Chemical Corporation, New Haven, Connecticut

In a previous paper¹ we have described a study of the absorption of glycerol by gel cellulose regenerated from viscose solution. This work was done at 20° with the use of a bath containing 10.0% glycerol. Our results indicated little or no enrichment of glycerol solution by the film during the sorption process, thus casting doubt on the existence of a special affinity of cellulose for glycerol, as has been reported previously.² In the present paper, further experiments are described in which the examination of this enrichment problem is attacked in a somewhat different way. The range of glycerol concentration is extended also in the present work down to 3.8% and up to 95%.

EXPERIMENTAL PART

Materials

Gel Film. The material used was cellulose film regenerated from viscose. Two different samples were used. The degree of polymerization of the films was determined by viscosimetry in cupriethylenediamine solution and was found to be 430 for sample A and 550 for sample B. The film was stored in rolls submerged in distilled water in a refrigerator.

Glycerol. Reagent-grade glycerol from Allied Chemical Corporation was used as softener. The concentration of the stock glycerol was between 95 and 96%, and it was checked each time before use.

Preparation of Film Samples

A piece of gel film was cut (usually 10 × 12 cm.), and the excess water on the surface was removed by blotting with paper towels. The sample was put into a weighing bottle and the total weight of the film equilibrated in pure water was determined. Then the sample was placed in a beaker of

aqueous glycerol of the desired concentration and covered tightly with polyethylene film to prevent evaporation of water from the bath. The amount of liquid in the bath was 50 to 100 times greater than the weight of the film, and therefore the decrease in the glycerol concentration was small.

After some preliminary measurements had revealed difficulties in securing reproducible results, improvements in handling and weighing were made. The samples were carefully equilibrated, blank runs were made, and corrections were applied to compensate for the amount of water unavoidably lost by evaporation during handling.

Since it was important to be certain that equilibrium had been reached, at least within the limit of accuracy of other measurements, i.e., within 0.2% (the limit of reproducibility of the concentration measurements), several precautions were taken, as follows. (a) The equilibration time was several hours. Several special runs were made to see how long it took to reach equilibrium. A film sample immersed in glycerol solution was suspended on a Westphal balance. This permitted the change in weight to be used as a direct observation of approach to equilibrium. The weight change on the balance showed how closely equilibrium had been approached. At lower glycerol concentrations (up to 40%), no further change in weight could be observed after 20 minutes. This time was enough for practical equilibration at low concentrations. (b) Equilibrium was approached from both sides in some experiments, i.e., from both higher and lower concentrations of glycerol. A film sample containing no glycerol was immersed in a bath and the equilibrium concentration measured. The sample then was placed in a highly concentrated solution, where it picked up a large amount of glycerol. Later it was returned to the first solution of lower glycerol content. The equilibrium concentration in this second procedure was found to be the same as in the first. (c) To improve the access of glycerol to the film the bath was stirred, and from time to

* At the time when this work was done, a member of the Cellulose and Colloid Chemistry Department; at present associated with the Energy Division.

time the sample was lifted out and allowed to drain. This procedure was found to be important at glycerol concentrations higher than 60%, because the solutions are very viscous and diffusion is slow. (d) In the experiments done with 95% glycerol (the most concentrated solution available), the liquid was so viscous that the precautions just mentioned seemed to be insufficient. Therefore the bath and film sample were heated to approximately 70° for several hours. At this temperature the viscosity is about one-twentieth that at room temperature. The bath was taken out of the oven and cooled to 25°. After standing again at room temperature for several hours, the sample was assumed to have reached equilibrium.

Blank runs were made to correct for substances that might be extracted and calculated as glycerol in analysis. The extracts from the blanks showed a slightly greater refractive index than that of water, indicating that some substances in the gel film, perhaps oligosaccharides or other degradation products, are extracted in the Soxhlet extractor. From the refractive index of the blanks the amount of these substances was calculated as glycerol, the assumption being that they effect the same change in refractive index as glycerol. This amount was 0.2% based on the gel film and 0.7% based on the oven-dry cellulose. Because of the presence of extractables, all glycerol determinations were 0.2% too high, and all results presented herein have been corrected accordingly.

Because of the large area-to-volume ratio of gel film, exposure to air results in rapid loss of water, and it was deemed necessary to determine this rate loss and not to be misled by it. Film samples were taken from the bath, blotted quickly to remove excess liquid from the surface, folded, and placed in weighing bottles. Thus, during this procedure some water evaporates, which causes a change in the composition of the film so that the water content drops and the glycerol content appears to be higher. To avoid this error, special care was taken to prevent exposure of the equilibrated film to the air as much as possible. The samples were exposed to air for no more than 30 sec. In addition, a series of experiments was made to measure the evaporation rate of water and to calculate the possible error arising from it. A film sample was suspended on the balance and the rate of evaporation measured by the loss in weight at regular intervals. The balance case was kept open to avoid accumulation of water vapor inside. The temperature was 25° and relative humidity, 64%. Under these conditions the

weight of the film decreased 2%/min. in the first few minutes after the film was taken from the water and the excess of water removed. Calculations based on the exposed film surface showed that 0.1 mg. of water evaporates each minute from a fresh film for each square centimeter of surface exposed. (This rate decreases to approximately one half of the initial value after 30 min.)

Experiments were made also to measure the evaporation rate of water and glycerol solutions from the liquid surface in an open dish. The results given in Table I show that water in a dish evaporates 2.4 times faster than from a cellulose film gel. Water-glycerol solutions evaporate more slowly the higher the glycerol concentration. At 84% glycerol, equilibrium with 64% relative humidity prevails, and at higher concentrations of glycerol the solution absorbs water from the air. These data were used to apply corrections to all measured concentrations to compensate for evaporation. The correction in no case exceeded 0.5%.

TABLE I
Rate of Loss of Water from Gel Film and Glycerol Solutions
at 25° and 64% Relative Humidity^a

| Sample | Glycerol concentration, % | Rate of evaporation, mg./cm. ² /min. |
|-------------------|---------------------------|-------------------------------------------------|
| Gel film | 0 | 0.098 |
| Water | 0 | 0.235 |
| Glycerol solution | 3.8 | 0.227 |
| Glycerol solution | 6.7 | 0.215 |
| Glycerol solution | 16.1 | 0.194 |
| Glycerol solution | 39.9 | 0.140 |
| Glycerol solution | 59.2 | 0.095 |
| Glycerol solution | 75.1 | 0.046 |
| Glycerol solution | 84.7 | -0.001 (hygroscopic) |
| Glycerol solution | 95.2 | -0.079 (hygroscopic) |

^a Under conditions of free evaporation.

Analysis of Film Samples

The films were weighed in a weighing bottle and transferred to a Soxhlet extractor for extraction with water. The extract was concentrated by evaporation, weighed, and the glycerol concentration was determined by measuring the refractive index. From the amount of extract and the concentration, the glycerol content of the samples was calculated.

After extraction of glycerol the cellulose content was determined by drying the extracted film for several hours at 105°. The amount of water in each sample was obtained by difference.

The concentration of glycerol in the softener bath

in equilibrium with the film was determined by refractive index.

Refractive Index of Water-Glycerol Solutions at 25°

A standard temperature of 25° was used for equilibration of film samples and measurements of refractive index were made also at this temperature. Since a complete table of refractive indexes of aqueous glycerol solutions is available only for 20°⁵ and the values for 25° given by Iyer and Usher³ are incorrect (the refractive index of water measured by them does not agree with the accepted value, being 8 units too high in the fourth decimal place), a new calibration table was constructed of refractive indexes of solutions of water and glycerol at 25°.

A series of standard solutions was prepared containing glycerol of different known concentrations, 0, 5, 10, 15, 20, 25, 30, 40, 50, and 95.2%, made by mixing weighed amounts of water and glycerol stock solution containing 95.2% glycerol. The concentration of the stock solution was determined by measuring density, refractive index at 20°, and viscosity. Then the refractive indexes of the standard solutions were measured at two different temperatures, 20 and 25°. The accuracy of the refractometer readings was within ± 0.0001 .

The values of refractive indexes at 25° were obtained also by calculation by the Lorentz-Lorenz equation

$$r = (1/\rho)(n^2 - 1)/(n^2 + 2)$$

where r is a constant, ρ is the density, and n is the refractive index. The densities of glycerol solutions are given at both 20 and 25° by Bosart and Snoddy⁴ and the refractive indexes at 20° by Hoyt.⁵ From these data the refractive index at 25° could be calculated. In practice the difference between the two refractive indexes ($\Delta n = n_D^{20} - n_D^{25}$) was calculated from the differential form of the Lorentz-Lorenz equation:

$$\Delta n = 3\Delta\rho r/2n(1 - r\rho)^2$$

where $\Delta\rho$ is the difference in the densities at 20 and 25°. The calculations were made for different concentrations (in 5% steps) to the fifth decimal place.

The measured and calculated values agreed well, and were used as a basis for making a complete conversion table (Table II). In Table II, the third column shows the difference of the indexes of each

TABLE II
Refractive Index of Aqueous Glycerol Solutions at 25°

| Glycerol, wt.-% | n_D^{25} | Difference $\times 10^5$ | |
|--------------------|------------|--------------------------|----------|
| | | per 1% | per 1°C. |
| 0 | 1.33254 | | 10 |
| 5 | 1.33830 | 115 | 10 |
| 10 | 1.34429 | 120 | 10 |
| 15 | 1.35049 | 124 | 11 |
| 20 | 1.35686 | 127 | 11 |
| 25 | 1.36335 | 130 | 13 |
| 30 | 1.36993 | 131 | 15 |
| 35 | 1.37658 | 133 | 16 |
| 40 | 1.38328 | 134 | 17 |
| 45 | 1.39012 | 137 | 18 |
| 50 | 1.39716 | 141 | 19 |
| 55 | 1.40446 | 146 | 21 |
| 60 | 1.41186 | 148 | 23 |
| 65 | 1.41926 | 148 | 24 |
| 70 | 1.42671 | 149 | 24 |
| 75 | 1.43416 | 149 | 24 |
| 80 | 1.44167 | 150 | 25 |
| 85 | 1.44938 | 154 | 28 |
| 90 | 1.45708 | 154 | 27 |
| 95 | 1.46467 | 152 | 26 |
| 100 | 1.47264 | 159 | 27 |

per cent of glycerol for interpolation, and the fourth column the temperature correction for each degree in the range between 20 and 25°. (In applying the temperature correction, it should be noted that for rising temperatures the refractive index decreases.)

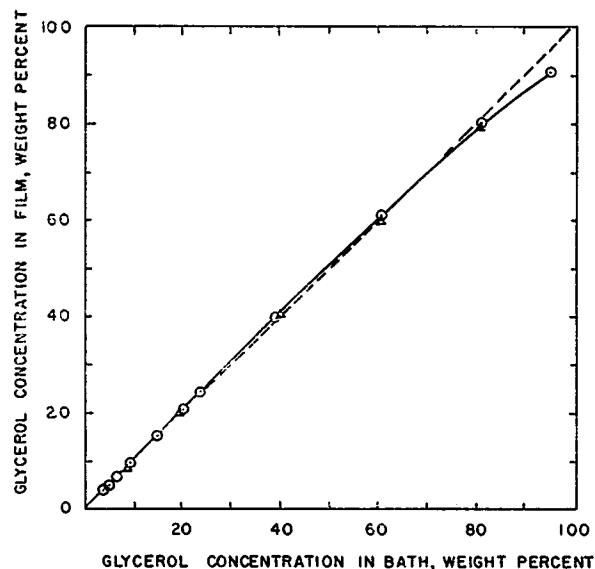


Fig. 1. Concentration of glycerol in films equilibrated with glycerol solutions at 25°: (○) film A; (△) film B; (—) calculated on the assumption of no enrichment of glycerol in softened regenerated cellulose film.

TABLE III
Composition of Gel Film in Aqueous Glycerol Solutions
(Temperature 25°)

| Sample | Glycerol concentration, wt.-% | | | Enrichment factor c_2/c_1 | Water and glycerol in film, % based on cellulose | Composition of gel film, wt.-% | | |
|--------|-------------------------------|---------------|-------------|-----------------------------|--------------------------------------------------|--------------------------------|-------|----------|
| | In bath c_1 | In film c_2 | $c_2 - c_1$ | | | Cellulose | Water | Glycerol |
| Film A | 0 | 0 | 0 | | 344 | 22.5 | 77.5 | 0 |
| | 3.8 | 3.8 | 0 | 1.00 | 369 | 21.3 | 75.7 | 3.0 |
| | 4.6 | 4.6 | 0 | 1.00 | 364 | 21.5 | 74.9 | 3.6 |
| | 6.7 | 6.7 | 0 | 1.00 | 356 | 21.9 | 72.9 | 5.2 |
| | 9.5 | 9.5 | 0 | 1.00 | 355 | 22.0 | 70.6 | 7.4 |
| | 15.0 | 15.1 | 0.1 | 1.01 | 375 | 21.0 | 67.1 | 11.9 |
| | 20.1 | 20.8 | 0.7 | 1.03 | 362 | 21.7 | 62.0 | 16.3 |
| | 23.7 | 24.5 | 0.8 | 1.03 | 390 | 20.4 | 60.1 | 19.5 |
| | 39.2 | 40.2 | 1.0 | 1.02 | 385 | 20.6 | 47.5 | 31.9 |
| | 60.7 | 61.0 | 0.3 | 1.01 | 424 | 19.1 | 31.5 | 49.4 |
| | 80.8 | 80.2 | -0.6 | 0.99 | 485 | 17.1 | 16.4 | 66.5 |
| | 94.6 | 91.0 | -3.6 | 0.96 | 410 | 19.7 | 7.2 | 73.1 |
| | Film B | 0 | 0 | 0 | | 322 | 23.7 | 76.3 |
| 9.1 | | 9.1 | 0 | 1.00 | 333 | 23.1 | 69.9 | 7.0 |
| 19.9 | | 20.6 | 0.7 | 1.03 | 329 | 23.3 | 60.9 | 15.8 |
| 39.3 | | 40.5 | 1.2 | 1.03 | 366 | 21.5 | 46.7 | 31.8 |
| 60.5 | | 60.3 | -0.2 | 1.00 | 397 | 20.1 | 31.8 | 48.1 |
| 80.6 | | 79.6 | -1.0 | 0.99 | 491 | 16.9 | 16.9 | 66.2 |

RESULTS OF EXPERIMENTS

The experiments were all done in duplicate from 3.8 to 94.6% glycerol in the bath, and for the two different gel films A and B. The data are presented in Table III, together with calculated enrichment factors. The tabulated results are each an average of at least four experiments, except for one ($c_1 = 94.6\%$) which is a single experiment. Errors arising from extractable substances and from evaporation described above have been corrected for. The same data are presented in Figures 1 and 2.

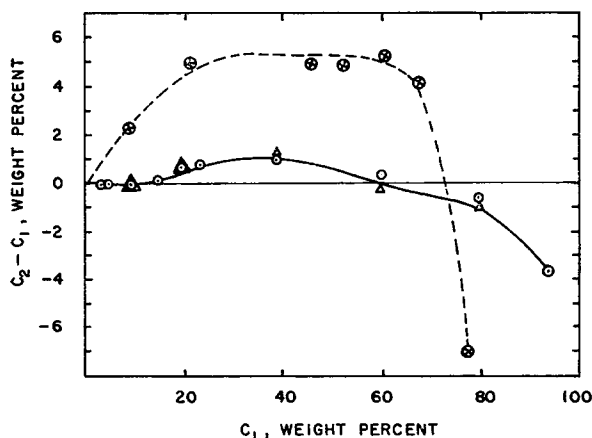


Fig. 2. Difference in glycerol concentration in cellulose films and glycerol baths ($c_2 - c_1$) as a function of glycerol concentration in the bath c_1 : (○) film A; (△) film B. The results of Danilov *et al.*² (⊕) are included for comparison.

DISCUSSION OF RESULTS

The results show that there is a very small difference between the concentration of glycerol in the film and the concentration of glycerol in the corresponding equilibration bath. The solid line of Figure 1 connecting the experimental points is nearly indistinguishable from the broken line representing $c_1 = c_2$, i.e., a condition of no enrichment. At glycerol concentrations below 16% no difference could be detected. At higher concentrations, a small positive difference appears (enrichment of glycerol in the film), which reaches a maximum in the enrichment factor at 20–25% concentration of glycerol and then decreases to zero at 60–70% glycerol. At still higher concentrations, enrichment is reversed (the bath solution outside the film is richer in glycerol than the liquid inside the film). Thus cellulose exerts no clear preferential affinity for glycerol in aqueous solutions.

No difference in the behavior of the two different films A and B was found, though the degree of polymerization of the two was not the same. In Figure 2 are shown for comparison the experimental results of Danilov, Sokolovskii, and Evdokimova.² They found a strong preferential absorption of glycerol at all concentrations up to 70%.

Column 5 in Table II shows the enrichment factor, i.e., the ratio of c_2 to c_1 . Column 6 shows the amount of liquid, i.e., the weight of water and glycerol, absorbed by 100 parts of cellulose.

Columns 7, 8, and 9 show the composition in weight-per cent of all three components (cellulose, water, and glycerol) inside the film when it is in equilibrium with bath solution c_1 .

Glycerol and water are evidently absorbed by cellulose in practically the same ratio as they occur in bath solution. At all concentrations of glycerol from 4 to 95%, the enrichment observed is very small. Of commercial importance are softener baths that contain glycerol in concentrations lower than 20%, and, in this concentration range, preferential absorption is negligible. Therefore, in practice it can be assumed that the glycerol solution inside the film has the same concentration as in the bath, provided equilibrium conditions are reached.

The great enrichment of glycerol in film observed previously² may perhaps be explained by the presence of impurities in the film, such as degradation products of cellulose, which would give the same analytical reaction as glycerol. Oxidation by dichromate was used to determine glycerol, blank runs were not mentioned, and it may be assumed therefore that no corrections were made for additional substances which may have affected the glycerol determinations.

The inversion of the absorption at high glycerol concentrations has been explained by assuming the presence of glycerol trihydrate (63.01% glycerol) in the region where the inversion takes place.² The assumption of the existence of definite chemical hydrates of glycerol, i.e., of compounds having a fixed composition, rests upon studies made many years ago⁶ in the infancy of our ideas of association by hydrogen bonding in liquids. The evidence adduced at that time for the existence of hydrates of definite composition was not very convincing then and is unacceptable today.

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Synopsis

The absorption of glycerol solutions by cellulose regenerated from viscose has been studied over a range of glycerol concentrations up to 95%. After corrections had been made for loss of moisture in handling, only very small differences between the concentration of glycerol in the film and the concentration of glycerol in the equilibration bath were found. The enrichment factor (defined as the ratio of glycerol concentration in the film to the glycerol concentration in the bath) was unity up to 16% glycerol, reached a maximum of 1.03 at approximately 25% glycerol, and fell to 0.96 at 95% glycerol concentration. We concluded therefore that glycerol and water are absorbed by gel cellulose in practically the same ratio as they occur in the bath solution and no preferential affinity for glycerol over water is evident. Two cellulose films of different degree of polymerization gave similar results. A redetermination of refractive indexes of aqueous glycerol solutions at 25° is included.

Résumé

L'absorption de solutions de glycérine par la cellulose régénérée à partir de viscose a été étudiée dans un domaine de concentrations de glycérine allant jusqu'à 95%. Après corrections pour la perte d'humidité durant la manipulation, seules de très petites différences ont été trouvées entre les concentrations de glycérine dans le film et dans le bain à l'équilibre. Le facteur d'enrichissement (défini comme le rapport de concentration en glycérine dans le film à la concentration en glycérine dans le bain) est égal à un jusqu'à 16%, atteint un maximum de 1,03 vers 25% en glycérine et retombe à 0,96 à 95% de glycérine. Nous concluons donc que la glycérine et l'eau sont absorbés par le gel de cellulose dans des proportions pratiquement identiques à celles du bain, et qu'il n'y a pas d'affinité préférentielle pour la glycérine ou l'eau. Deux films de cellulose de différents degrés de polymérisation donnent des résultats similaires. On a également redéterminé les indices de réfraction d'une solution aqueuse de glycérine à 25°.

Zusammenfassung

Die Absorption von Glycerinlösungen durch Cellulose, die aus Viskose regeneriert worden war, wurde über einen Bereich von Glycerinkonzentrationen bis zu 95% untersucht. Nach Anbringung einer Korrektur für den Feuchtigkeitsverlust während der Behandlung wurden nur sehr kleine Unterschiede zwischen der Konzentration des Glycerins im Film und der Konzentration des Glycerins in der Gleichgewichtslösung festgestellt. Der Anreicherungs faktor (definiert als Verhältnis der Glycerinkonzentration im Film zu der Glycerinkonzentration im Bad) war bis zu 16% Glycerin gleich eins, erreichte ein Maximum von 1,03 bei etwa 25% Glycerin und fiel bei einer Glycerinkonzentration von 95% auf 0,96 ab. Man kam daher zu dem Schluss, dass Glycerin und Wasser von Gelcellulose in praktisch dem gleichen Verhältnis absorbiert werden, in dem sie in der Lösung vorhanden sind und dass kein Anzeichen für eine bevorzugte Affinität für Glycerin gegenüber Wasser besteht. Zwei Cellulosefilme mit verschiedenem Polymerisationsgrad lieferten ähnliche Ergebnisse. Eine Neubestimmung der Brechungsindizes wässriger Glycerinlösungen bei 25° wird mitgeteilt.

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