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Volume Changes During Glycerol Absorption by Regenerated Cellulose

ROMAN MYKOLAJEWYCZ,* ORVILLE J. SWEETING, and EMIL CZAPEK,† *Film Operations, Packaging Division, Olin Mathieson Chemical Corporation, New Haven, Connecticut*

In previous reports on the mechanism of softener absorption by regenerated cellulose[1–4] studies were referred to that were made in this laboratory of the changes in volume which are observed when a cellulose gel absorbs glycerol from aqueous solutions of glycerol over a wide range of concentrations. In this paper the details of these experiments are described.

Experimental

Materials and Methods

The cellulose gel film samples and glycerol used were the same as previously reported.[2] A careful comparison was made of the volume of the softened gel films and the sum of the volumes of the components, cellulose and aqueous glycerol, over the range of 10 to 80% in the softener bath.

Procedure

Gel film samples were immersed in aqueous glycerol solutions of known concentration (Table I) until equilibrium had been achieved. The samples were then suspended on the Westphal balance and the weights of each in air and in the respective softener baths were determined. The specific gravity of the bath solution was determined using a standard plummet, and the values were compared with the values in the literature.[5] The specific gravity of glycerol was redetermined.[2] From the data, the volume of the softened film samples was calculated.

The volume of dry cellulose was determined from the oven-dry weight and the specific gravity. The latter was found by matching with the density of test liquid mixtures not appreciably absorbed by cellulose. The liquids used were carbon tetrachloride (ρ_{25} = 1.585 g./ml.) to which small amounts of chloroform (ρ_{25} = 1.487 g./ml.) or acetone (ρ_{25} = 0.79 g./ml.) were added as required. Several such solutions were used, and the density of each was accurately determined with the Westphal balance. Small

* At the time when this work was done, a member of the Cellulose and Colloid Chemistry Department.

† Deceased.

TABLE I
Density and Volume Changes in Softened Gel Cellulose Films

Glycerol concn. in bath, wt.-%	Density of softened film, g./cc. at 25°C.	Volume contraction in gel formation, %		Swelling of gel when softened, %	
		From dry cellulose and aqueous glycerol[a]	From dry cellulose, water, and glycerol	Wt. increase of gel upon softening, %	Vol. increase of gel upon softening, %
		Film Sample A			
0	1.090	0.81		0	0
9.6	1.109	0.97	1.16	2.8	1.0
21	1.130	0.74	1.14	6.1	1.9
41	1.174	0.67	1.42	9.3	2.8
61	1.218	0.79	1.68	17.9	5.4
80	1.258	0.70	1.41	28.5	11.7
		Film Sample B			
0	1.094	0.89		0	0
9.6	1.113	0.74	0.93	2.6	1.0
21	1.135	0.98	1.38	5.3	1.8
41	1.179	0.70	1.43	10.2	2.6
61	1.219	0.62	1.50	17.7	5.7
80	1.255	0.52	1.19	31.7	12.5

[a] Compare Table III of ref. 2.

pieces of cellulose were immersed until the densities agreed; the density found was 1.528 ± 0.002 g./cc.

Finally the samples were analyzed for water and glycerol content, thus allowing a computation to be made of the theoretical volumes which would be occupied by the three components of the softened films taken separately.

Results

In Table I the results of the experiments described have been summarized. (Samples A and B represent cellulose of different degrees of polymerization.[2]) The volume contraction (column 3) has been calculated as a percentage of the sum of the theoretical original volumes of the film components, i.e., by considering the films as constituted from dry cellulose plus aqueous glycerol. It will be noted from these data and the plotted values in Figure 1 that the difference in volume of the final system and the volume of cellulose plus *glycerol solution* is small at all concentrations studied, in all cases less than 1%, with an average of approximately 0.7%.

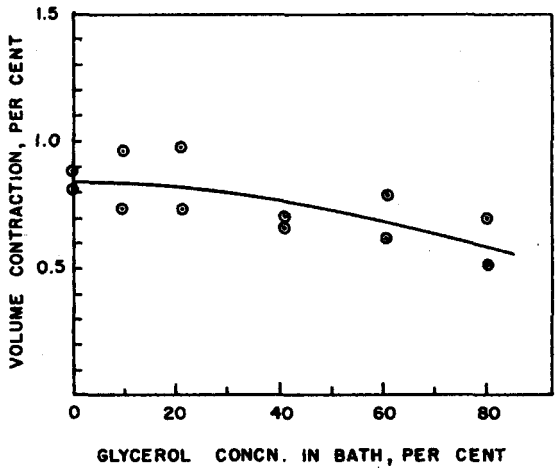

Fig. 1. Volume contraction of gel cellulose as a function of glycerol concentration in the softener bath.

In column 4 is tabulated the volume contraction from the standpoint of the volume of the final system compared with the volumes of cellulose plus glycerol plus water taken separately. This result agrees well with the known effects observed upon mixing water and glycerol in various proportions.[6] Thus the softened cellulose system does not behave unlike a cellulosic body containing simply glycerol solutions, i.e., a mixture of polymer and *glycerol solutions*.

Nothing said above is to be misconstrued in connection with what happens to a sample of wet gel cellulose when it is immersed in aqueous glycerol solutions. The last two columns of Table I gave the corresponding values for weight and volume increases which gel cellulose has been found to

undergo when immersed in glycerol solutions from 10 to 80% concentration It is seen that at concentrations below 20% the swelling effect of glycero solutions on cellulose gels is small, no more than 2%, which is in general agreement with preliminary data reported.[1]

Discussion

The nearly constant internal contraction over the whole range of softener concentrations probably should be ascribed to strong hydrogen bonding of water to cellulose. At very high glycerol concentrations the volume contractions decreased slightly, possibly because glycerol is preferentially held to the cellulose chains. These data justify the tentative conclusion made earlier[1] that the internal volume contractions for softened and unsoftened gel film are the same and that therefore a direct comparison of volume of water and of water-softener solution based on the densities can be made.

The slow gradual increase in total volume of gel film with increasing softener content found, mainly occurring at glycerol concentrations greater than 50%, must be ascribed to a gradual increase in free volume caused by additional uptake of water by the hygroscopic softener which, at the high softener concentrations, becomes adsorbed on the surface of the cellulose. This swelling effect is time dependent and is observed only after equilibration times of several hours.

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Synopsis

The volume changes which a cellulose gel swollen with water undergoes on immersion in aqueous glycerol solutions containing from 10–80% glycerol have been studied. If the gel is considered from the standpoint of dry cellulose plus glycerol solution, the volume contraction (compared with the theoretical sum of the volumes of the components) is less than 1% over the entire range of glycerol concentrations studied. When the unsoftened gel film is immersed in softener solution, the volume increase of the gel is small (1–5%, corresponding to a concentration of 10–60% glycerol in the softener bath). It may therefore be concluded that, except possibly at very high glycerol contents, the internal volume relationships for softened and unsoftened gel film are the same.

Résumé

On a étudié les variations de volume subies par un gel de cellulose gonflé dans l'eau lors de l'immersion dans des solutions aqueuses contenant 10 à 80% de glycérine. Si le gel est étudié du point de vue de la somme cellulose sèche plus la solution de glycérine,

la contraction de volume (comparée à la somme théorique des volumes des composants) est inférieure à 1% pour le domaine des concentrations étudiées. Lorsque le film d'un gel non ramolli est immergé dans une solution qui facilite le ramollissement, l'augmentation de volume du gel est faible (1–5%, correspondant à une concentration en glycérine de 10–60% dans le bain ramollissant). Nous pouvons par conséquent conclure, sauf probablement pour des teneurs en glycérine très élévées, que les relations de volume interne d'un film de gel ramolli ou non sont les mêmes.

Zusammenfassung

Es wurde die Volumsänderung untersucht, die ein in Wasser gequollenes Cellulosegel bei Immersion in Glycerin–Wasserlösungen mit einem Glyceringehalt von 10 bis 80% erfährt. Bezogen auf trockene Cellulose plus Glycerinlösung ist die Volumskontraktion (verglichen mit der theoretischen Summe der Volumina der Komponenten) im gesamten untersuchten Bereich an Glycerinkonzentrationen weniger als 1%. Wenn der nicht weichgemachte Gelfilm in Weichmacherlösung getaucht wird, so ist der Volumszuwachs des Gels gering (1–5%, entsprechend einer Konzentration von 10–60% Glycerin im Weichmacherbad). Wir dürfen daher schliessen, dass, ausser eventuell bei sehr hohem Glyceringehalt, die Beziehungen für das innere Volumen für weichgemachten und nicht weichgemachten Gelfilm dieselben sind.

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