

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF OREGON]

THE STRUCTURE OF CELLULOSE ACETATE GELS FROM STUDIES OF DIFFUSION

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The structure of gels of gelatin and agar-agar has been the subject of earlier investigation by one of the authors.¹ This paper is a report of studies made on the gel system cellulose acetate in benzyl alcohol, which was chosen for study in order that the structural investigations might be carried out in the absence of water. By this means the possibility of structural modification resulting from the presence of ions and from contamination of the gels by molds was avoided. As a further precaution against changes of the original structure during the investigations, methyl and ethyl alcohol were selected as diffusates because of their negligible degrees of ionization in benzyl alcohol and the fact that cellulose acetate is insoluble in either.

Method and Materials.—The method of studying diffusion employed in this work was that developed by Friedman and Kraemer,¹ for their study of gelatin and agar-agar systems. In this method, a mass of material, the diffusate, is dissolved in a given mass of the dispersing medium of the gel. A volume of this solution just equal to the volume of the gel to be studied is placed upon the gel and kept stirred. The diffusate penetrates into the gel, the extent of diffusion as a function of time being determined at appropriate intervals.

The equation connecting the diffusion coefficient with the time-concentration data in the liquid layer was developed for this particular method by March and Weaver.² In its expanded form, it becomes

$$V = \frac{1}{2} - [0.327e^{-4.117T} + 0.0766e^{-24.14T} + 0.0306e^{-63.66T} + 0.0160e^{-123T} + \dots] \quad (1)$$

V is the fraction of the material that has diffused into the gel at a given time. $T = Dt/a^2$, where D is the coefficient of diffusion, t is the time in seconds, and a is the height of the gel layer and also that of the liquid layer.

By substituting values for T , it was possible to plot a theoretical curve. To determine the value of the diffusion coefficient, D , for a given system, the value of T corresponding to the experimentally determined value of V is read from the theoretical curve. Then the value of D is calculated from the equation $D = a^2T/t$.

The cellulose acetate used was a chemically pure product obtained from the Eastman Kodak Company and received no treatment beyond

¹ Friedman and Kraemer, *THIS JOURNAL*, **52**, 1295 (1930).

² March and Weaver, *Phys. Rev.*, **31**, 1072 (1928).

sufficient mixing to ensure its homogeneity. Cellulose acetate, although insoluble in water, is of a porous nature, and it was found necessary to remove the adsorbed moisture in an electric oven at 92°. The loss amounted to from 2 to 2.5% by weight. Since water is only very slightly soluble in benzyl alcohol, no drying of the chemically pure solvent, benzyl alcohol, also obtained from the Eastman Kodak Company, was attempted.

Experimental Procedure

Sols of various concentrations were prepared by heating the proper mixtures of cellulose acetate and benzyl alcohol for one hundred fourteen minutes at 100°. The sols were permitted to gel in a thermostat at 25° and after thirty-six hours, a time interval sufficient to ensure complete gelation, a diffusate solution was placed upon the respective gels and the diffusion studies were started. The changes in concentration of the diffusate were measured by tracing the refractive index changes of the solution and the calculation of the diffusion coefficients made as described above. An example of the results obtained is shown in Table I.

TABLE I

DIFFUSION OF METHYL ALCOHOL INTO A CELLULOSE ACETATE GEL

3% methyl alcohol solution. 15% cellulose acetate. Area of bottle, 20.83 sq. cm. Total shift, 23.57.

| Time in minutes | Refractometer shift | V | T | $D \times 10^*$ |
|-----------------|---------------------|--------|---------|-----------------|
| 1399 | 2.41 | 0.1023 | 0.00965 | 0.2376 |
| 1545 | 2.52 | .1081 | .01092 | .2434 |
| 1700 | 2.62 | .1112 | .01166 | .2367 |
| 2037 | 2.81 | .1192 | .01360 | .2299 |
| 2744 | 3.23 | .1371 | .01870 | .2347 |
| 2872 | 3.31 | .1405 | .01971 | .2364 |
| 3043 | 3.40 | .1443 | .02080 | .2354 |
| 3152 | 3.46 | .1468 | .02170 | .2371 |
| 3251 | 3.56 | .1510 | .02300 | .2436 |
| 3434 | 3.64 | .1544 | .02420 | .2427 |
| 4296 | 3.87 | .1642 | .02810 | .2254 |

Average 0.2366

Effect of Concentration of Gel on Rate of Diffusion.—To show the effect of concentration of cellulose acetate upon the gel systems studied, determinations of the rates of diffusion were made upon gels of concentrations ranging from 2 to 20% cellulose acetate by weight. The numerical results obtained are shown in Table II and are plotted in Fig. 1.

The diffusate in Runs I, II, and III was C_2H_5OH from a 10% solution; in Run IV from a 3% solution; in Run V, CH_3OH from a 3% solution.

A study of the curves (Fig. 1) reveals that the diffusion coefficient is a linear function of the cellulose acetate concentration. The values of the coefficients for the various runs indicate the impossibility of reproducing a

TABLE II
DIFFUSION COEFFICIENTS $\times 10^5$ versus CONCENTRATION OF GELS

| Concn. of gel, % | I | II | Run No. III | IV | V |
|------------------|--------|--------|-------------|--------|--------|
| 20 | 0.0635 | | 0.1081 | | |
| 17.5 | | | | | 0.0719 |
| 15 | | 0.1016 | | 0.1158 | |
| 12 | | .1368 | | .1369 | .1482 |
| 10 | .1279 | | .2337 | | |
| 9 | | .1550 | | .1738 | |
| 7.5 | .1481 | | .2866 | | .1854 |
| 6 | | .1957 | | .2029 | .1958 |
| 5 | .1680 | | .3134 | | |
| 4 | | .2273 | | .2377 | |
| 2.5 | .2024 | | .3686 | | .2484 |

given system with exactitude. This may be attributed either to the inevitable slight differences in the thermal treatment of the gels of one run from that of another or to the impossibility of even a statistical control of the incomplete or imperfect crystallization that results in gel formation.

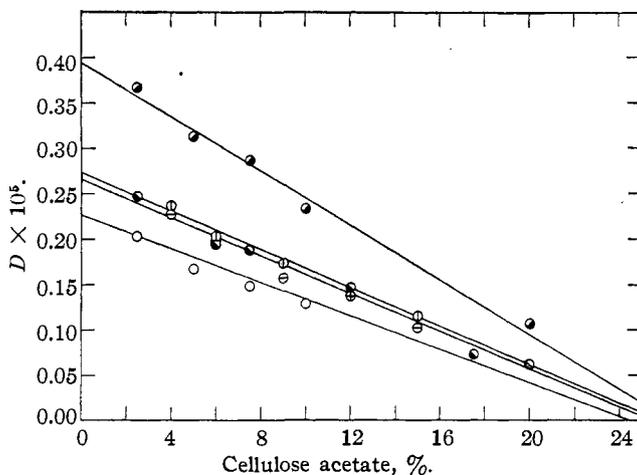


Fig. 1.—Diffusion in cellulose acetate gels: ○, Run no. I; ⊖, Run no. II; ●, Run no. III; ⊕, Run no. IV; ●, Run no. V.

Determination of the Effective Pore Radii.—In the determination of the effective average pore radius of a given gel the formula derived by Friedman and Kraemer was used,¹ which for these determinations takes the form

$$D_{alc.} = D_{gel} \cdot (1 + \alpha) \cdot (1 + \pi) \cdot (1 + 2.4r/R) \tag{2}$$

$D_{alc.}$ is the diffusion coefficient of the diffusate in benzyl alcohol. D_{gel} is the diffusion coefficient of the diffusate in a given gel system at the same concentration of diffusate employed in determining $D_{alc.}$. α is the correc-

tion factor for the viscosity and is equal to the quotient of $D_{\text{alc.}}$ divided by D_{gel} extrapolated to zero concentration of cellulose acetate. π is the correction for mechanical blocking and is calculated from Dumanski's formula:³ $\pi = \sqrt[3]{(g/d)^2}$ where g is the number of grams of cellulose acetate in 1 cc. of gel, and d is the density of the cellulose acetate. $(1 + 2.4r/R)$ is an approximation for the determination of the average pore size. It was taken from Ladenburg's correction for the fall of bodies in capillary tubes and was originally intended to be applied to Stoke's Law. r is the radius of the diffusate molecule and R is the effective average radius of the pores in the gel.

The values of the diffusion coefficients for methyl and ethyl alcohol in benzyl alcohol at 25° and in the concentrations used in the experiments were not extant and were determined by the method devised by Northrop,⁴ and perfected and standardized by McBain and Liu.⁵

This method depends upon the separation, by means of an indifferent membrane with pores of microscopic size, of two homogeneous bodies of solution. In this way the diffusion gradient is confined within this membrane. The results obtained are relative but are standardized by the measurement of a single standard solution the absolute value of whose diffusion coefficient is known at some definite concentration and temperature.

The equation relating the diffusion coefficient of a given system to the time during which diffusion occurs was derived from Fick's equation, $ds = DA(dc/dx)dt$, and takes the form

$$KD = \frac{\log C_0 - \log (C_0 - 2C)}{t} \quad (3)$$

K is the cell constant. C_0 is the original concentration of the diffusate within the cell used. C is the concentration of diffusate outside the cell at a given time. D is the diffusion coefficient of the diffusate at the concentration and temperature of the experiment. t is the time elapsed between the beginning and end of the diffusion. The values so obtained are shown in Table III.

TABLE III

DIFFUSION COEFFICIENTS OF CH₃OH AND C₂H₅OH IN BENZYL ALCOHOL AT 25°

| Diffusate | CH ₃ OH | C ₂ H ₅ OH | C ₂ H ₅ OH |
|----------------------|--------------------|----------------------------------|----------------------------------|
| Concn. (% by weight) | 3 | 3 | 10 |
| $D \times 10^6$ | 0.8144 | 0.8080 | 0.5463 |

By substitution of the values in Table III into equation (2) the values given in Table IV were obtained.

³ Dumanski, *Kolloid-Z.*, **3**, 210 (1908).

⁴ Northrop and Anson, *J. Gen. Physiol.*, **12**, 543 (1929).

⁵ McBain and Liu, *THIS JOURNAL*, **53**, 58 (1931).

TABLE IV

EFFECTIVE PORE RADII IN $m\mu$ IN GELS OF DIFFERENT CONCENTRATIONS

| Run no. | Concentration of gel as percentage cellulose acetate | | | | |
|-----------|--|-------|-------|--------------------|-------|
| | 2% | 5% | 10% | 15% | 20% |
| I | 17.451 | 5.928 | 1.621 | 0.638 | 0.213 |
| II | 18.195 | 5.996 | 1.732 | .711 | .263 |
| III | 19.894 | 6.186 | 1.883 | .792 | .306 |
| IV | 17.497 | 5.882 | 1.795 | .747 | .291 |
| V | 17.918 | 5.551 | 1.553 | .633 | .234 |
| Mean | 18.191 | 5.909 | 1.717 | 0.704 | 0.261 |
| Max. dev. | 9% | 6% | 10% | 12 $\frac{1}{2}$ % | 18% |

Discussion of Results

By plotting the pore radii as ordinates against the concentrations as abscissas (Fig. 2), the pore radii are seen to approach $18 m\mu$ at 2% concentration of cellulose acetate and $0 m\mu$ at 23% gel. However, the pore openings would be expected to become discontinuous at a concentration below 23%, providing the preparation of a homogeneous gel of such concentration were not beyond experimental realization.

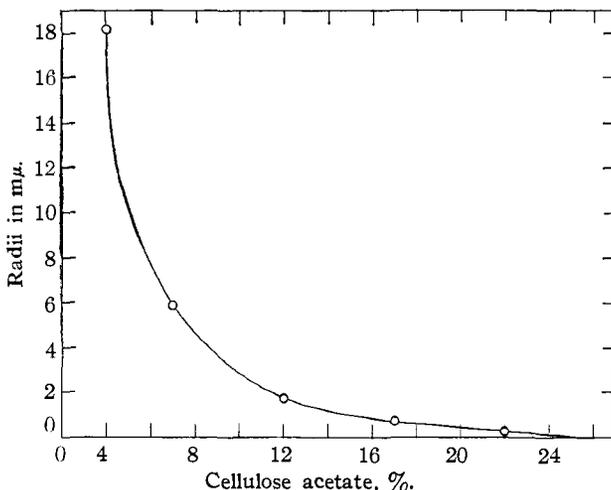


Fig. 2.—Change of pore radii with concentration.

The employment of the theoretical diffusion curve developed by March and Weaver² for the work of Friedman and Kraemer¹ gives a constant diffusion coefficient at any time interval for a given gel, even in such diverse systems as gelatin in water, agar-agar in water, and cellulose acetate in benzyl alcohol. This strongly supports the validity of the diffusion equation employed in the investigation and the values of the coefficients obtained.

It is considered that the above results, if not conclusive proof of the liquid-solid theory of gel structure, are at least very strong evidence in favor of the theory.

That the rate of diffusion decreases with increased gel concentration is in support of the pore theory, since the effective pore radii would be expected to decrease with increased concentration of the dispersed medium until the pores should become discontinuous.

The high values of the determined diffusion coefficients are inconsistent with those to be expected in a solid solution where, as a result of the enormous increase of the viscosity of the system upon gelation, diffusion should practically cease.

The change in magnitude of the pore radii with change in the concentration of cellulose acetate is seen from Fig. 2 to be an exponential function. This is in accord with the liquid-solid theory, which infers a change of effective pore radius with change in concentration. Any change in effective pore radius must be followed by a change in the number of pores within a given volume of gel. Since gel formation is conceded to be an incomplete precipitation of the dispersed medium, the resulting pore openings might be considered as consisting of minute tubes of varying lengths, chaotically arranged, but each intersecting others to form continuous open passages completely through a gel. The thickness of the pore walls is also undoubtedly a function of the concentration. That the radii and the number of the pore openings change with concentration has been demonstrated by this investigation. The fact that approximate equations for the experimentally determined curve, Fig. 2, obtained by the method of least squares lead to curves more nearly symmetrical with the experimental curve as the number of terms (and consequently the degree of the function) increases, supports the postulates mentioned above.

Summary

1. A study of the structure of gels of cellulose acetate in benzyl alcohol has been made by measuring diffusion into the gels with time.
2. It has been shown that the diffusion law holds for the penetration of the employed diffusates into cellulose acetate gels.
3. The validity of the diffusion equation employed in the investigation has been supported by the diffusion coefficients obtained.
4. The values of the effective pore radii of gels of various concentrations have been determined and found to be of the same order of magnitude as those obtained by Friedman and Kraemer for gelatin and agar-agar systems.
5. The high values of the experimentally determined diffusion coefficients render untenable the solid solution theory of gels.
6. The change in pore radii with change in concentration has been shown to be an exponential function, a rate of change to be expected in the liquid-solid theory.