

[CONTRIBUTION FROM THE COLLOID LABORATORY, UNIVERSITY OF WISCONSIN]
STRUCTURE OF AGAR GELS FROM STUDIES OF DIFFUSION¹

BY LEO FRIEDMAN

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Although agar forms a gel very readily and is quite easily handled, the investigations of diffusion in gels seem, for the most part, to have been carried out in gelatin systems. Voigtlander^{1a} studied the diffusion of four electrolytes in agar gels at 20° and came to the conclusion that the diffusion constant is independent of the concentration of gel. Bechhold and Ziegler² paralleled their studies in gelatin with some in agar, finding a 15% decrease in the rate of diffusion of the juice of red beet as the concentration of agar was increased from 1 to 4%. Fricke,³ while developing his micro-slicing method, made a few determinations of the diffusion of sodium chloride in agar, but no extensive studies were made of the properties of the agar systems.

Experimental

The agar used in these studies was the ordinary commercial material carefully purified by preliminary soaking in acetic acid and water, followed by electro dialysis. This purification process, however, removing most of the electrolytes also destroyed some of the gelling properties of the agar, for as the iso-electric point is approached the gel becomes less stable.

The procedure followed in the determination and calculation of the diffusion constants was the same as that used in the studies on gelatin.⁴ Because of the fact that agar does not stick to glass it was necessary to line the bottles with a Bakelite varnish which adhered closely to the glass and to which the agar would stick.

Effect of Concentration of Gel on Rate of Diffusion.—To show the effect of concentration of agar upon the structure of the gels, determinations of the rates of diffusion of urea and glycerin were made in various concentrations of purified gels. Curve a, Fig. 1, shows the diffusion of urea in agar gels. Between the concentrations of 0.8 and 5.15% the diffusion is slowed down 36%, in contradiction to the work of Voigtlander. Curve b, Fig. 1, shows the diffusion of glycerin in agar gels.

Dimensions of the Gel Framework in Agar Gels.—Using the same equations and methods as in the calculations for gelatin,⁴ the size of the openings in the solid framework of agar gels has been calculated from the curves in Fig. 1. The results of these calculations are shown in Table II. The larger values for the radii from the glycerin determinations would be

¹ An extract from a thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy, University of Wisconsin.

^{1a} Voigtlander, *Z. physik. Chem.*, **3**, 316 (1889).

² Bechhold and Ziegler, *ibid.*, **56**, 105 (1906).

³ Fricke, *Z. Elektrochem.*, **31**, 430 (1925).

⁴ Friedman and Kraemer, *THIS JOURNAL*, **52**, 1295 (1930).

TABLE I
DIFFUSION IN AGAR GELS VS. CONCENTRATION OF GEL

Agar concn., %	Total diff., hours	Expts.	Diffusion constants ($K \times 10^3$)		Mean
			Max.	Min.	
(a) Urea into the gel from a 3% solution					
0.79	46	8	0.777	0.690	0.740
1.05	51	10	.797	.617	.727
1.11	18	3	.757	.707	.739
1.50	49	11	.845	.544	.694
1.58	48	10	.777	.570	.691
1.64	18	3	.736	.695	.710
2.39	49	8	.622	.554	.582
3.16	17	3	.670	.530	.591
3.16	48	10	.662	.465	.590
4.08	49	9	.609	.461	.518
5.15	48	10	.500	.442	.472
(b) Glycerin into agar from a 3% solution					
2.06	33	8	0.322	0.281	0.297
3.01	33	10	.426	.123	.272
3.91	33	10	.295	.192	.244
6.02	33	10	.245	.138	.199

expected from the tremendous effect which glycerin has on the agar. In the latter part of this paper it is to be noted that glycerin increased the rate of diffusion of urea in agar by 50%, which means that it had modified the structure to allow this faster diffusion.

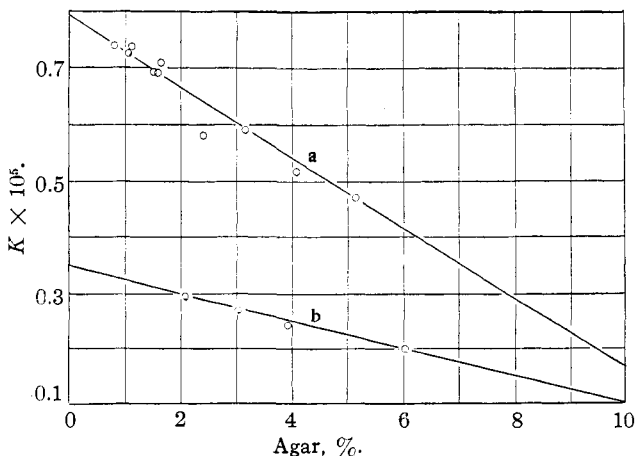


Fig. 1.—Diffusion in agar gels.

The order of magnitude of the radii of the pores in the agar gels is the same as that found for gelatin gels. However, the pores are decidedly smaller in the agar gels, as would be expected from the fact that a 1% agar gel is about as strong physically as a 5% gelatin gel.

TABLE II
SIZE OF THE PORES IN AN AGAR GEL

Substance diffusing	Urea	Glycerin
Radius of pores { 2% gel	2.9m μ	5.65m μ
{ 5% gel	0.74m μ	1.43m μ

Diffusion of Non-Electrolytes in Agar.—It was found in the work on gelatin gels⁴ that the rate of diffusion of a non-electrolyte was determined to

TABLE III
DIFFUSION OF VARIOUS NON-ELECTROLYTES IN AGAR GELS

Diffusing substance	$\frac{1}{\sqrt{\text{Mol. wt.}}}$	Total diff., hours	Diffusion constants ($K \times 10^5$)			
			Expts.	Max.	Min.	Mean
(a) Diffusion into 0.79% gel from 3% solutions						
Urea	0.129	50	10	0.693	0.546	0.629
Trimethylene glycol	.115	48	8	.470	.392	.439
Dextrose	.075	50	10	.369	.292	.327
Sucrose	.054	50	11	.306	.197	.247
(b) Diffusion into 5.15% gels from 3% solutions						
Ethyl alcohol	0.148	47	9	0.527	0.282	0.393
Urea	.129	48	10	.500	.442	.472
Propyl alcohol	.129	48	10	.563	.244	.330
Pyridine	.113	48	10	.362	.202	.316

a large extent by the molecular weight or size of the diffusing molecule, although it also was influenced by the specific effect of that non-electrolyte on the gelatin. Similar studies have been carried out with agar gels.

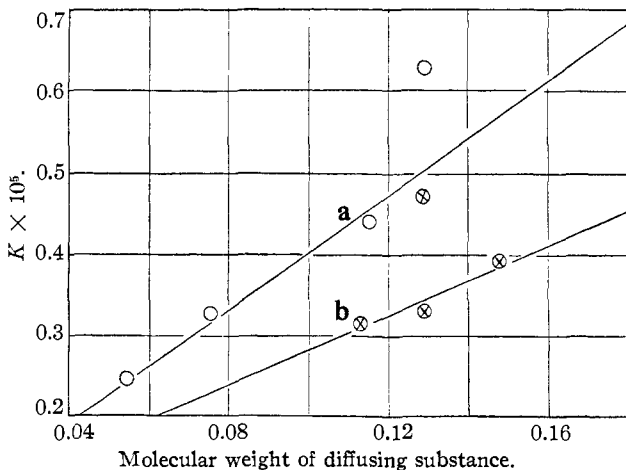


Fig. 2.

Curve a, Fig. 2, shows the diffusion of four non-electrolytes in 0.8% agar gels. Corrected values were not calculated,⁴ because the agar used for these studies was electrodyalized to a different extent than that used for the

studies of the effect of the non-electrolytes discussed later. Curve b, Fig. 2, shows the diffusion of four non-electrolytes in a 5.15% agar gel. The relation that $K^2 \times M = \text{a constant}$ is indicated but the variation is quite large. The specific action of the non-electrolyte upon the agar is too great to permit drawing any more quantitative conclusions.

Effect of Non-Electrolytes on Rate of Diffusion.—To determine the effect of various non-electrolytes on the diffusion process in agar gels, experiments similar to those performed with gelatin were carried out.⁴ It was found that ethyl alcohol alone, of those non-electrolytes used, decreased the rate of diffusion of urea in agar, whereas glycerin, dextrose and trimethyleneglycol caused enormous increases, as shown in Table IV.

TABLE IV
EFFECT OF NON-ELECTROLYTES UPON DIFFUSION OF UREA INTO AGAR GELS FROM A 3% SOLUTION

Substance present in the gel	Total diff. hours	Expts.	Diffusion constants ($K \times 10^3$)			Increase in rate for urea, %
			Max.	Min.	Mean	
Diffusion into 1.5% gels						
.....	49	11	0.845	0.544	0.694	..
Ethyl alcohol	48	10	.796	.420	.646	-6.9
Glycerin	48	11	1.100	.891	1.036	49.3
Lactose	48	10	0.827	.583	0.739	6.5
Sucrose	48	11	.825	.503	.714	2.9
Diffusion into 3% gels						
.....	45	11	0.524	0.418	0.470	..
Methyl alcohol	46	10	.585	.405	.531	13.0
Urea	26	6	.603	.375	.518	10.2
Trimethyleneglycol	46	10	.928	.597	.697	48.2
Dextrose	46	10	.975	.714	.809	72.0

Summary

1. A study of the diffusion of non-electrolytes in gels of agar has been made; diffusion coefficients for several non-electrolytes have been determined.
2. It has been shown that the rate of diffusion in agar gels decreases linearly as the concentration of gel increases.
3. The possible dimensions of the gel framework have been calculated from the rates of diffusion of non-electrolytes in the gels.
4. The relation between the molecular weight of the diffusate and its rate of diffusion in the gel has been shown to be the same as in a liquid medium.
5. The effect of various non-electrolytes upon the structure of the gel framework has been investigated through their influence on the rate of diffusion of a single diffusate.