motions of the pendant vinyl groups prevent the reaction from going to completion. For cases wherein the activities of the vinyl groups are similar, a theory has been presented by which predictions of the cross-linking efficiency can be made, at least for copolymers containing more than about 5 or 10 mole per cent. of the divinyl monomer. Although the theory in its present preliminary form is based on a simplified model, nevertheless it provides an analytical expression which satisfactorily represents the observed dependence of the efficiency on the degree of cross-linking and on the length of the cross-linker. This is of great practical utility since we are thereby enabled to predict the efficiency curve for copolymers of MMA with the dimethacrylates of similar structure but of different length, *e.g.*, *it was possible in the present case from the observed efficiency curve for EGDMA to predict accurately the curve for DGDMA before any measurements were made on the latter system.* It is expected that the range and systems for which reliable predictions can be made will be extended by future theoretical and experimental work.

In those copolymers wherein the extent of cross-linking is limited by the onset of the glassy state during polymerization, quantitative prediction of the cross-linking efficiency awaits a more detailed knowledge of the factors which determine the temperature at which glass formation occurs.[7]

Acknowledgments.—We acknowledge the constant inspiration of Dr. J. F. Kincaid throughout the course of this work. We are also indebted to Dr. Serge Gratch, who aided with the theoretical calculations; Dr. J. D. Stroupe, who performed the infrared analyses; Mr. N. DiCandilo, who assisted with the experimental work; and Drs. J. L. O'Brien, C. H. McKeever, E. H. Kroeker and Mrs. M. Gluckman, who prepared the various divinyl monomers.

PHILADELPHIA, PA.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Measurement of Ordinary Diffusion Coefficients of Polymers[1]

BY F. T. WALL AND C. W. CHILDERS

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Ordinary diffusion coefficients have been measured for several polymers using a method involving diffusion from a porous frit. The validity of the experimental method was checked by comparison with free boundary diffusion measurements on polyvinyl alcohol, dextran, and bovine serum albumin. The diffusion of polyacrylic acid was also investigated in relation to its ionization.

A great variety of physical-chemical measurements have been carried out for the purpose of characterizing polymer molecules in solution. Of the various properties so measured, that of ordinary diffusion has been relatively neglected, mainly because of the difficulty of obtaining accurate values of that quantity. Although the significance of an ordinary diffusion coefficient is evident, its measurement is often unsatisfactory because of the slow rate at which polymer molecules diffuse. Recently, however, a rapid method for measuring diffusion coefficients of substances in solution was described.[2] This method involves saturating a porous disc with the solution to be investigated and then suspending the disc in a large bath of solvent. From a knowledge of the apparent weight of the suspended disc as a function of time, it is possible to deduce the extent of diffusion from the disc and to calculate, by simple graphical means, the ordinary diffusion coefficient of the solute.

The idea of diffusion into a porous material was employed previously by Aten and v. Dreven,[3] but they did not determine the extent of the diffusion by weighing a suspended disc. The present authors have recently learned, however, that Schulze[4] used the change in buoyant force technique nearly 40 years ago to follow movement out of a frit, although he was not concerned with high molecular weight substances.

The purpose of the present paper is to report results obtained by the frit method for some polymers in solution. Some of the results are also compared with data obtained by an optical method with generally good agreement.

Experimental

The apparatus and technique employed were the same as previously described[2] except that the solvent container was placed in a large constant temperature bath. In addition, solvent was kept covered to prevent cooling by evaporation; this precaution was particularly important when volatile organic solvents were employed.

Porous plates which had been soaked with polymer solution were suspended in the bath of solvent from one arm of an analytical balance, and the apparent weight was measured as a function of time. If W is the absolute value of the difference between the apparent weights at time t and after a long (infinite) time, then the asymptotic slope of the line obtained by plotting log W *vs.* t is proportional to the diffusion coefficient. A characteristic frit constant, K, is determined by calibration so that the diffusion coefficient D can be obtained from the aforementioned slope by the simple relationship

$$D = -K \times \text{slope}$$

Values of the frit constants were determined by carrying out diffusion experiments on aqueous potassium chloride solutions. Using the value 2.91×10^{-5} cm.^{2}/sec. for the diffusion coefficient of 0.1 N HCl[5] at 25°, frit no. 1 (see Table I) was found to have a characteristic constant equal to 17×10^{-4}. Further experiments using 0.5 N KCl for

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[1] The work discussed herein was supported in part by the research project sponsored by the Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the Government Synthetic Rubber Program.

[2] F. T. Wall, P. F. Grieger and C. W. Childers, THIS JOURNAL, **74**, 3562 (1952).

[3] A. H. W. Aten, Jr. and J. v. Dreven, *Trans. Faraday Soc.*, **44**, 202 (1948).

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each of the fritted discs (including no. 1) made possible the complete set of calibrations shown in Table I.

TABLE I

Disc no.	Thickness in mm.	$-$Slope $\times 10^2$	$-$Slope $\times 10^2$ average	$K \times 10^4$
1	4.25	1.111, 1.10, 1.13	1.12	17.0
5	1.10	10.0, 10.3, 10.1	10.1	1.89
9	1.06	10.9, 11.0	11.9	1.73
10	1.12	9.62, 9.84	9.7	1.96
11	0.95	14.0, 14.1, 14.0	14.0	1.36
12	1.05	12.1, 11.6, 11.8	11.8	1.61
13	1.00	12.2, 12.5, 13.0	12.6	1.51

Although the validity of our experimental method appeared established for low molecular weight materials, some question might be raised with respect to high polymeric substances. To check this possibility, three polymeric materials (polyvinyl alcohol, dextran and bovine serum albumin) were investigated both by the frit method and by the free boundary procedure using a Tiselius type cell,[6] with results shown in Table II. Even though the agreement is not all one might hope for, there is no evidence of a systematic difference which might be attributed to inherent weaknesses in the method. The weight time data for an experiment using polyvinyl alcohol are shown in Fig. 1; the calculated points were obtained by substituting the measured slope into the complete theoretical expression.[2] The experimental points at short times do not agree with the exact analytical solution but they do approach a straight line at the predicted time. It is assumed that the initial rapid change in weight is caused by excess solution remaining on the frit and that an appreciable time is required before it is completely washed away.

TABLE II

COMPARISON OF DIFFUSION COEFFICIENTS OBTAINED USING THE FRIT METHOD AND THE FREE BOUNDARY TECHNIQUE FOR THREE POLYMERS AT 25°

Substances	Diffusion coefficient $\times 10^7$ Frit method	Free boundary
3.5% Polyvinyl alcohol in water	2.46, 2.64	2.74
1.5% Dextran in 0.7 *M* NaCl	5.4	5.1
0.7% Bovine serum albumin in buffer	7.4	7.2

It might also be supposed that change of solvent would render invalid the calibration of a fritted disc, so the data of Gerlach[7] on the diffusion of benzene in carbon tetrachloride were used to test this possibility. His value for this diffusion coefficient (corrected to 25°) is compared in Table III with our results, which were computed assuming validity of the aqueous calibration. Although our results are somewhat higher on the average, there is no basis for supposing that the aqueous calibration must be seriously in error.

TABLE III

DIFFUSION COEFFICIENT OF AN 8.8% SOLUTION OF BENZENE IN CARBON TETRACHLORIDE DIFFUSING INTO CARBON TETRACHLORIDE AT 25°

Frit no.	$D \times 10^5$, cm.^{2}/sec.
5	1.77, 1.76
9	1.57, 1.73
10	1.77
Gerlach[7]	1.61

Results on Polyacrylic Acid

We were interested in obtaining a value for the diffusion coefficient of un-ionized polyacrylic acid so that its molecular weight might be determined (from a combination of sedimentation and diffusion data) for comparison with a light scattering value.

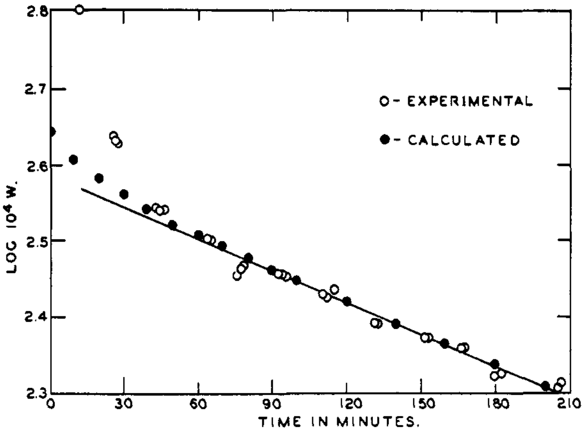

Fig. 1.—Plot of log *W* *vs.* time for 3.5% polyvinyl alcohol dissolved in water.

Since polyacrylic acid is ionized in aqueous solution, the rapid diffusion of the hydrogen ions tends to pull along the large negatively charged polymer ions. As a result, the diffusion of ionized polymer is more rapid than that for an uncharged molecule of equal size.

An attempt was first made to suppress the ionization of polymeric acid by adding HCl. As shown in Table IV, the diffusion coefficient decreases with increasing hydrochloric acid concentration.

TABLE IV

VARIATION OF DIFFUSION COEFFICIENT OF 4.6% POLYACRYLIC ACID IN PRESENCE OF HCl

HCl concn., *N*	Diffusion coefficient of polyacrylic acid $\times 10^7$, cm.^{2}/sec
0.0	46.4
.05	4.9
.1	3.7
.5	2.8
1.0	2.0

Measurements could not be made in solutions of HCl more concentrated than 1.0 *N* because of the effect on the solubility of the polyacrylic acid.

A change in solvation of the polymer molecules may be responsible for the relatively small decreases in *D* accompanying increases in HCl concentration above 0.05 *N*. It cannot be assumed that there is no ionization, however, since *D* still has not leveled off at the highest added acid concentration employed.

A solvent suitable for measuring diffusion of uncharged polyacrylic acid is dioxane. The measured diffusion coefficients of polyacrylic acid in water–dioxane mixtures (Table V) are fully con-

TABLE V

DIFFUSION COEFFICIENTS OF 4.6% POLYACRYLIC ACID IN DIOXANE–WATER MIXTURES

Mole % of dioxane in solvent	$D \times 10^6$, cm.^{2}/sec.	$D\ \eta/\eta_0 \times 10^6$, cm.^{2}/sec.
0	4.64	3.57
2.3	2.26	2.18
5.0	1.01	1.17
8.3	0.66	0.84
17.4	.44	.71
33.0	.37	.60
100	.21	.21

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[6] We are indebted to Mr. J. J. Scholz of this Laboratory for the free boundary diffusion measurements.

[7] B. Gerlach, *Ann. Physik*, **10**, 437 (1931).

sistent with the assumption that there is little or no ionization of the acid in dioxane.

The diffusion coefficient decreases rapidly as the dioxane content of the solvent changes from zero to 20 mole per cent. From this point on to pure dioxane, D decreases slowly even though the dielectric constant decreases rapidly.[8] The values in the last column of Table V represent diffusion coefficients corrected to the viscosity of pure dioxane so as to provide a uniform basis for comparison. The correction factor equals the quotient of the viscosity of the mixture by the viscosity of pure dioxane (η/η_0). This correction is necessary because the viscosity of water–dioxane mixtures varies with concentration and passes through a maximum at 20 mole per cent. dioxane.[8]

Conductance measurements likewise give the expected evidence that there is little ionization of polyacrylic acid in dioxane. The data of Table VI show that the specific conductance of polyacrylic acid in dioxane–water mixtures exhibits the same type behavior as the diffusion coefficient. The conductance data also have been corrected to the viscosity of pure dioxane.

TABLE VI

SPECIFIC CONDUCTANCE, λ, OF POLYACRYLIC ACID IN DIOXANE–WATER MIXTURES

Mole % of dioxane in solvent	Weight % polyacrylic acid	$\lambda \times 10^6$	$\lambda\ \eta/\eta_0 \times 10^6$
0.0	0.845	555	420.7
2.29	.850	322.3	296.6
5.0	.852	174.7	191.7
8.22	.842	89.7	115.1
12.20	.838	42.1	62.3
17.22	.837	18.0	29.0
23.62	.832	4.0	6.7

The partial specific volume and the sedimentation constant of polyacrylic acid in dioxane were also measured. The values were 0.69 ml. and 4.03 $\times 10^{-13}$ sec., respectively. The molecular weight calculated from these data combined with the diffusion coefficient is 1.6×10^5 which is to be compared with a light scattering value of 2.3×10^5, also measured in this Laboratory. Since different kinds of averages of the molecular weights are involved, the agreement is satisfactory.

Experiments also have been carried out on other polymers such as fractions of polystyrene and fractions of polyisobutylene. The results will not be reported at this time, however, since the measurements were made at one concentration only. The expected dependence in molecular weight was observed for both materials.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Dipole Moments and Structures of *cis*- and *trans*-1,2-Dichlorocyclohexane[1,2]

BY A. TULINSKIE, A. DI GIACOMO[3] AND C. P. SMYTH

RECEIVED MARCH 12, 1953

The dipole moments of *cis*- and *trans*-1,2-dichlorocyclohexane have been measured in the vapor state and in benzene solution. The values obtained for the *cis* isomer correspond closely to a 1e,2p configuration, while those for the *trans* show the substance to be an equilibrium mixture of 1e,2e and 1p,2p configurations. The energy difference between the two configurations is calculated and the effect of the solvent upon the energy of the polar configuration is shown.

Pure samples of *cis*- and *trans*-1,2-dichlorocyclohexane prepared[4] by Dr. Henry C. Stevens and Professor Oliver Grummitt of Western Reserve University and sent to us for dipole moment determinations have made possible an investigation of the structure and relative stabilities of the different molecular forms of these compounds.

Experimental Methods and Results

The dipole moments of the molecules were measured in benzene solution and in the vapor state. The refractive indices n^{20}_D reported[4] for the two 1,2-dichlorocyclohexanes were *cis*, 1.4968; *trans*, 1.4904. Our values were *cis*, 1.49684; *trans*, 1.49039. Benzene purified as in earlier work[5] boiled at 80.2° (765 mm.) and had a refractive index, n^{20}_D, 1.50132. The measurements of the dielectric constants and densities of the solutions in benzene were made by methods previously employed in this Laboratory,[5,6] as were the measurements on the vapors,[7] which, because of the high boiling points of the liquids, were made at only one temperature. Six or seven solutions of each substance were measured at concentrations from 0.0008 to 0.006 mole fraction of polar component. The polarizations P_∞ at infinite dilution were calculated by the Debye method and by that of Halverstadt and Kumler[8] from the constants of the equations for the dielectric constants ϵ_{12} and the specific volumes v_{12} as linear functions of the weight fractions w_2 of the solute

$$\epsilon_{12} = \epsilon_1 + \alpha w_2; \qquad v_{12} = v_1 + \beta w_2$$

The dipole moments were calculated by means of the usual equation

$$\mu = 0.01281 \times 10^{-18}[(P_\infty - R_D)T]^{1/2}$$

in which R_D is the molar refraction for the D sodium line and T, the absolute temperature. The experimental results are given in Table I.

Discussion of Results

A considerable amount of evidence[9] based on

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[1] This research has been supported in part by the office of Naval Research. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

[2] This paper represents a part of the work to be submitted by Mr. A. Tulinskie to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Procter and Gamble Fellow in Chemistry.

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[7] J. H. Gibbs and C. P. Smyth, *ibid.*, **73**, 5115 (1951).

[8] I. F. Halverstadt and W. D. Kumler, *ibid.*, **64**, 2988 (1942).

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