Diffusion in Polyelectrolyte Solutions

RICHARD G. GRISKEY* and G. H. SEDAHMED,† *Newark College of Engineering, Newark, New Jersey 07102*

Synopsis

Diffusion in polyelectrolyte solutions was studied. The mass transfer was determined by an electrochemical technique which involved transport from the fluid to the tube wall. It was found that diffusion behavior depended on the ionic nature of the diffusing species. Neutral molecules showed an increase in diffusion coefficients. This was apparently due to both solvation of solvent molecules and extension of polymer molecules. Ionic diffusing species showed a decrease in diffusion coefficients. The greater the ionic strength, the greater the decrease. The effect was most likely due to ionic interaction with the polyelectrolyte molecules.

INTRODUCTION

Mass transfer in polymer solutions is complicated by the effect of the polymer on the diffusion coefficients of the diffusing solvents. A number of investigators have studied diffusion in polymer solutions. Included are the studies of Wang,[1] Clough, Behn, and Metzner,[2] and Li and Gainer.[3] All of these not only studied diffusion in polymer solutions per se, but also developed expressions for predicting diffusion coefficients.

Although progress has been made in understanding diffusion in polymer solutions, there still are some problem areas. One in particular is diffusion in polyelectrolyte solutions. Hansford and Litt[4] as well as Astarita, Osmers, and Metzner[5] found a different pattern of behavior for such diffusion. In addition, there also seemed to be an effect of the ionic nature of the diffusing species.

The present work has therefore undertaken to study more fully diffusion in polyelectrolyte solutions, with special emphasis on the ionic nature of the diffusing species.

## APPARATUS AND EXPERIMENTAL PROCEDURE

Mass transfer was studied by an electrochemical technique which involved transport of mass from the fluid to the tube wall. This method was preferable to the soluble tube wall technique, since the latter led to rough-

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* Present address: College of Engineering and Applied Science, University of Wisconsin-Milwaukee, Milwaukee Wisconsin 53201.

† Present address: Chemical Engineering Department, University of Alexandria, Alexandria, U.A.R.

TABLE I
Physical Properties of Solutions Studied

| CMC concn., wt-%	Viscosity, centipoises	Density, g/cc
0	1.208	1.057
1	3.966	1.067
1.25	4.777	1.070
1.75	7.819	1.075
2.2	12.44	1.079
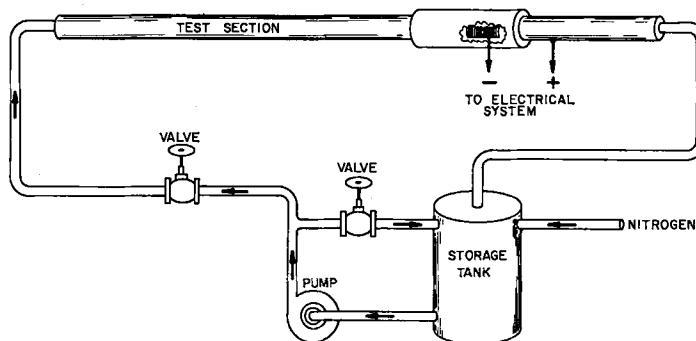
SCHEMATIC OF EQUIPMENT
Fig. 1. Schematic of equipment.

ness which interfered with mass transfer. The background of the electro-chemical technique has been described by Hanratty and co-workers.[6-8]

The actual rate of mass transfer in this work was determined by measuring the limiting current of the cathodic reduction of $K_3Fe(CN)_6$. The solutions used in the research were a blank solution ($0.025M$ $K_3Fe(CN)_6$ and $0.25M$ $K_4Fe(CN)_6$ in $1M$ NaOH) and polyelectrolyte solutions (blank solution plus a given ppm of polymer). The polyelectrolyte used in this work was carboxymethylcellulose sodium salt (H-K sodium CMC 110 g, a product of H. Kohnstamm and Company). The polymer was chemically stable under the conditions used in the present study.

Four concentrations of polymer solutions (1, 1.25, 1.75, and 2.2 wt-%) were studied. All solutions were Newtonian in flow behavior. Their densities and viscosities are given in Table I. The diffusion coefficient of ferricyanide ion was taken from the literature.

The investigation was carried out in the device shown in Figures 1 and 2. The mass transfer section was preceded by a nickel tube 200 diameters long. This tube segment served as an entrance section so that there would be hydrodynamically fully developed flow at the cathode. The electrochemical reaction took place (Fig. 2) between the cathode (a $5/8$-in.-long nickel ring) and the anode (a 3-ft-long nickel ring). The cathode was separated electrically both from the entrance section and the anode by poly(vinylchloride) rings.

B CATHODE (L/D=1)
C ANODE (36" LONG)
POLYVINYLCHLORIDE
NICKEL
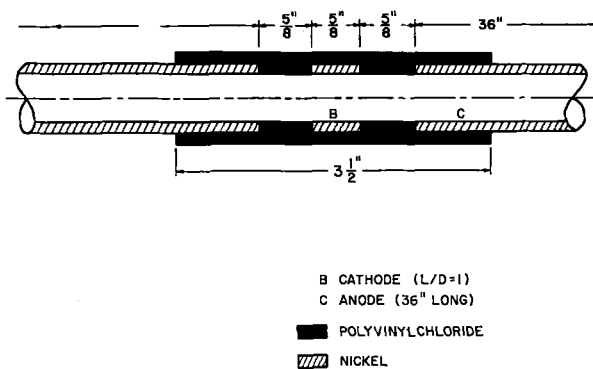
DETAIL OF TEST SECTION
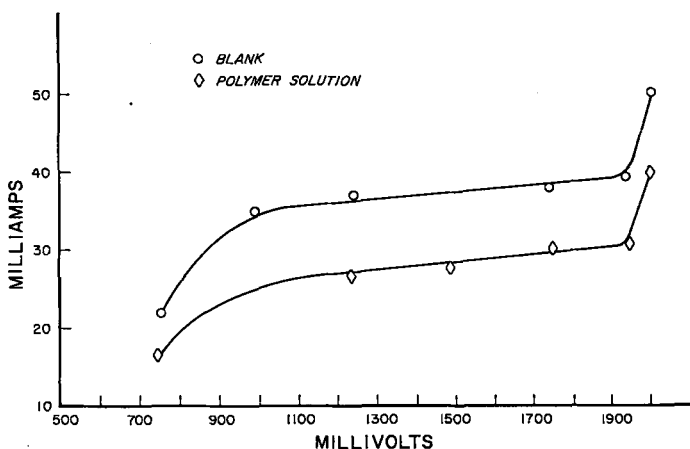
Fig. 2. Detail of test section.

Fig. 3. Limiting current curves.

Before each run, the cathode was cleaned with carbon tetrachloride and buffed with rough paper. Next, the cathode was activated by treating it cathodically in a 5% sodium hydroxide solution at a current density of 20 milliamperes for about 10 min.

Limiting current for the cathode was determined by increasing applied potential stepwise and recording the corresponding current until a plateau was obtained on the current potential curve. These curves were similar in shape to those observed by Hanratty.[6-8] For such conditions the current is controlled by the rate of mass transfer of ferricyanide ion to the surface of the working cathode (where the ferricyanide concentration is zero). Mass transfer coefficients and rates were then obtained from the limiting current data using the relation

$$N = \frac{i}{ZFA} = KC.$$
(1)

The value of current used in eq (1) was at the midpoint of the plateau portion of the curves in Figure 3.

It should be noted that this overall technique was proved out in an earlier study of drag-reducing fluids.[9]

RESULTS

Experimental data are plotted in Figure 4 as log of the Stanton number versus log of the Reynolds number. These data show that the mass transfer followed the Leveque equation

$$St = 1.615 \, Sc^{-1/3} \, Re^{-1/3} \tag{2}$$

since a set of parallel lines with a slope of $-2/3$ was obtained. Values of Schmidt number were calculated from the experimental data and the Leveque equation. In turn, diffusion coefficients were then computed from the Schmidt numbers. Table II summarizes all of the data.

Note that the effect of the polyelectrolyte is to decrease the diffusion coefficient of the ferricyanide ion. Also note that the diffusion coefficient value in the range of polymer solutions studied remains about the same. This behavior will be discussed in detail in the section that follows.

TABLE II
Experimental Data

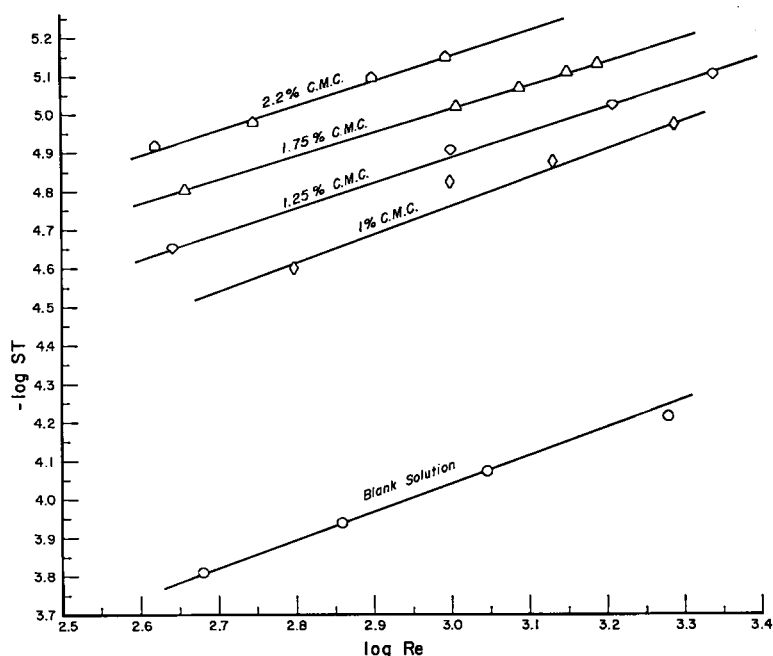| CMC concn., wt-%	Re	St × 10⁵	Sc	D, cm²/sec	D/D₀
0	480	15.47			
	735	11.3			
	1120	8.44			
	1910	5.98	2,220	5.15×10^{-6}	1.0
1	520	2.47			
	1000	1.48			
	1371	1.32			
	1962	1.03	31,620	1.1×10^{-6}	0.215
1.25	442	2.22			
	1110	1.2			
	1677	0.94			
	2221	0.75	43,370	1.03×10^{-6}	0.201
1.75	462	1.53			
	1035	0.91			
	1247	0.85			
	1434	0.77			
	1571	0.73	67,380	1.08×10^{-6}	0.211
2.2	422	1.21			
	562	1.04			
	808	0.79			
	983	0.56	114,100	1.01×10^{-6}	0.198

Fig. 4. Experimental data plotted as Stanton number vs. Reynolds number.

DISCUSSION

As was noted earlier, a different pattern of behavior was obtained for the two cases of diffusion in polyelectrolyte solutions in the literature. Astarita, Osmers, and Metzner[5] and Table III found that with neutral solute molecules, diffusion coefficients actually increased. On the other hand, Hansford and Litt[4] and Table IV determine that the diffusion coefficient of benzoic acid (a weak electrolyte) decreased with increasing polymer concentration. As a point of interest, the ratio D/D_0 (diffusion coefficient of the migrating species in a solution divided by diffusion coefficient in the pure solvent) is plotted against polymer concentration in Figure 5. As can be seen, there is a definite reduction in this ratio for both

TABLE III
Diffus on Coefficient of Various Solutes in Aqueous CMC Solutions[a]

Aqueous CMC solutions, wt-%	Temp., °C	Ethanol		Allyl alcohol		Glycerol	
		$D \times 10^5$ cm²/sec	D/D_0	$D \times 10^5$ cm/sec	D/D_0	$D \times 10$ cm/sec	D/D_0
0	23	0.98	1.0	0.84	1.0	0.93	1
0.5	23	1.23	1.3	0.94	1.1	1.06	1.1
1	23	1.55	1.6	0.97	1.2	1.14	1.2
2	23	1.50	1.5	0.97	1.2	1.21	1.30

[a] Data of Astarita, Osmers, and Metzner.

TABLE IV
Diffusion of Benzoic Acid in Aqueous CMC Solutions[a]

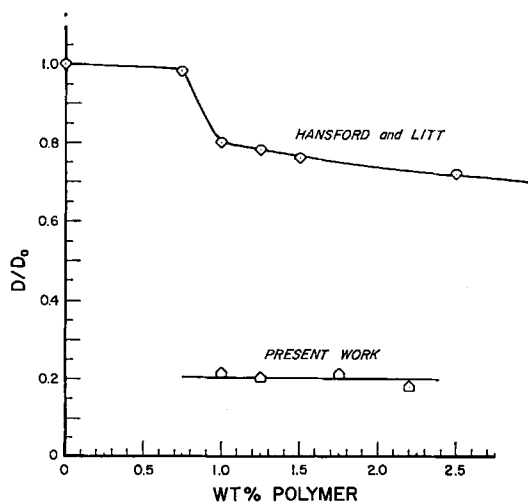| CMC solution, %	Temp., °C	D, cm²/sec $\times 10^5$	D/D_0
CMC 7HSP (0.75)	25	0.93	0.98
CMC 7HSP (1.00)	25	0.76	0.80
CMC 7HSP (1.25)	25	0.74	0.78
CMC 7HSP (1.50)	25	0.72	0.76
CMC 7MS (2.5)	25	0.68	0.72
CMC 7LP (6.4)	25	0.54	0.57

[a] Data of Hansford and Litt.[4]

Fig. 5. Relation of D/D_0 to polyelectrolyte concentration with ionic diffusing species.

the data of Hansford and Litt[4] and the present work. Note that the reduction in the present data is even more severe than that found by Hansford and Litt.[4] It should be reiterated that the ion in the present study is a much stronger electrolyte than the benzoic acid used by Hansford and Litt.[4]

Another interesting feature of Figure 5 is the apparent plateau or slow decrease in D/D_0 values that ranges from about 0.75% to 2.5% concentration. In essence, this behavior occurs with both weak and strong electrolytes.

Now let us consider the behavior of both the polyelectrolyte solution and the nature of the diffusing species so that the differences in behavior between the data of Astarita, Osmers, and Metzner,[5] Hansford and Litt,[4] and the present work can be explained.

As was noted, the diffusing species in the Astarita data was a neutral molecule. Hence, the sole effect there was that of the polyelectrolyte solution itself. When a polyelectrolyte is dissolved in a solvent, solvation of the polymer molecules occur. The effect of this solvation is to essentially remove a portion of the solvent molecules and increase the concentration

of the diffusing species. This tends to increase the diffusion coefficient of the diffusing species.

In addition, similarly charged segments of the polyelectrolyte molecule tend to repel each other. This results in an extended polymer molecule configuration. According to Wang,[1] diffusion of solutes with extended polymer molecules is easier than if the molecules are coiled. This improved diffusion situation also tends to increase the diffusion coefficient of the diffusing species.

It therefore appears that the increase in diffusion coefficients found by Astarita, Osmers, and Metzner[5] is most likely due to solvation of solvent molecules and extension of polymer molecules.

Consider next the case where the diffusing species is of an ionic nature. Here there will be interaction between the diffusing species and the polyelectrolyte molecules. One consequence of this interaction is to bring about a decrease in the repulsion between polymer molecules. The decreased repulsion tends to increase polymer molecule coiling[10] which in turn decreases the diffusivity of the migrating species.

In addition, there is the effect of electrolytes themselves in the diffusion coefficients of other electrolytes.[11] Such ionic interaction between the polyelectrolyte ions and the diffusing species ions results in a decrease of activity (effective concentration) of the diffusing species. This decrease reduces the value of the diffusion coefficient. The stronger the electrolyte nature of the diffusing species, the greater the decrease in the diffusion coefficient.

CONCLUSIONS

The conclusions from this study can be summarized as follows:

1. Diffusion behavior in polyelectrolyte solutions is dependent on the ionic nature of the diffusing species.

2. Neutral molecules show an increase in diffusion coefficient where the mass transfer takes place in polyelectrolyte solutions. This increase is due both to solvation of solvent molecules and extension of polymer molecules.

3. The diffusion coefficients of electrolyte species show a decrease in diffusion coefficient when mass transfer takes place in polyelectrolyte solutions. The degree of the decrease is dependent on the ionic strength of the diffusing species. This decrease in electrolyte diffusion coefficients is due to ionic interaction with the polyelectrolyte molecules.

Notation

i limiting current, amperes
A area of cathode, cm^2
C concentration, moles/cc
D diffusion coefficient in polyelectrolyte solution, cm^2/sec
D_0 diffusion coefficient in pure solvent, cm^2/sec

F Faraday's constant
N rate of mass transfer, moles/cm$^2\cdot$sec
Re   Reynolds number
Sc   Schmidt number
St   Stanton number
Z number of electrons involved in electrode reaction
ρ density, g/cc
μ viscosity, g/cm$\cdot$sec

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