

# Diffusion of Electrolytes in Dilute Polymer Solutions

G. H. SEDAHMED, M. A. EL-ABD, A. A. ZATOUT, and A. H. NEGM, *Chemical Engineering Department, Alexandria University, Alexandria, Egypt*

## Synopsis

The diffusion of sodium chloride in dilute solutions of carboxymethylcellulose (CMC) was studied using the porous frit technique. It was found that at relatively low CMC concentrations the diffusivity of sodium chloride ( $D$ ) is higher than that in water ( $D_0$ ); with increasing CMC concentration, the diffusivity decreases gradually and reaches a value lower than that in water. The relation between the diffusivity ( $D$ ) and CMC concentration ( $C_p$ ) was represented by the equation  $D = a - bC_p$ . The effect of temperature on the diffusivity of sodium chloride in CMC solutions was found to obey the Arrhenius equation with an activation energy of 2230 cal/mol.

## INTRODUCTION

Diffusion of electrolytes in polymer solutions is of importance in polymer production, processing, and application. In these processes it may be needed to dissolve an electrolyte in the polymer solution; sometimes an electrolyte has to be removed from the polymer solution for purification. To calculate the rate of such a process, electrolyte diffusivity in the polymer solution is needed. Also the problem is of interest to those concerned with the kinetics of polymerization or polymer modification in solutions containing electrolytes which may be added to catalyze the reaction or which may be produced during the reaction. The Robinson-Stokes equation<sup>1</sup> and the Onsager-Fouss equation,<sup>2</sup> which predict the diffusion behavior of electrolytes in concentrated and dilute electrolytes, respectively, fail to predict the diffusion behavior of electrolytes in polymer solutions because of the complex effects incurred by the presence of the polymer especially polyelectrolytes. Although some theories<sup>3-5</sup> have been introduced to account for the diffusion of low molecular weight solutes, none has found general validity. Most of the previous studies have concentrated on the diffusion of nonelectrolytes in nonionic polymers. The object of the present work is to shed some light on the diffusion of electrolytes in CMC solutions. The porous frit technique was chosen to conduct the present study in view of its rapidity, simplicity, and accuracy. The theory of the technique which has been used widely to study salt diffusion is presented elsewhere.<sup>6,7</sup>

## EXPERIMENTAL

A frit of unglazed porcelain of 10 mm thickness and 7 cm in radius which has been soaked with sodium-chloride solution for 24 h was suspended in a 30 L thermostated tank of CMC solution from one arm of an analytical balance

after draining off the excess salt solution clinging to the disc surface. The apparent weight of the disc ( $\omega$ ) was measured as a function of time ( $t$ ). The slope of the line obtained by plotting  $\log \omega$  vs.  $t$  is related to the diffusion coefficient of the salt ( $D$ ) by the equation:<sup>6,7</sup>

$$D = -K \times \text{slope} \quad (1)$$

The frit constant  $K$  was determined by carrying out diffusion experiments on 1 M aqueous potassium chloride whose diffusion coefficient is  $1.89 \times 10^{-5}$  cm<sup>2</sup>/s at 25°C.<sup>8</sup>

Following other authors<sup>6,7</sup> who used the technique, no correction was made for the buoyancy of the solution. Polymer adsorption on the disc surface was found to have no effect on  $\omega$ ; this was confirmed by soaking a disc saturated with distilled water in the polymer solutions for 24 h. No change in the disc weight ( $\omega$ ) was observed, indicating that polymer molecules could not diffuse through the disc pores. Diffusivity of sodium chloride in the concentration range 1.2–4.8M was measured in water and CMC solutions which ranged in concentration from 2 to 20 g/L. Rheological measurements revealed that all solutions used in the present work were Newtonian. Solution viscosity ( $\mu$ ) used in calculating the Einstein–Stokes ratio was determined using an Ostwald viscometer. Since all solutions were Newtonian, shear rate has no effect on the measured viscosity. All solutions were prepared using AR grade sodium chloride and distilled water. CMC used in the present study was provided by Hercules under the name “Hercules Cellulose Gum Type 7L.” The polymer has a molecular weight of 90,870, a degree of polymerization of 400, and a degree of substitution of 0.7. The diffusivity values measured in the present work represent the effective diffusivity of sodium chloride in aqueous CMC solutions which can be used directly in practice to predict rates of diffusion of sodium chloride in aqueous CMC solutions.

## RESULTS AND DISCUSSION

Figure 1 is a typical  $\log \omega$  vs. time used to obtain diffusion coefficient of sodium chloride under different conditions using Eq. (1). Figures 2 and 3 show the effect of CMC concentration on the diffusivity and diffusivity ratio of NaCl. At relatively low CMC concentrations the diffusivity of NaCl is higher than that in water; with increasing CMC concentration the diffusivity decreases gradually and reaches a value lower than that in water. To explain the diffusion behavior of NaCl in CMC solution, the properties of CMC as a macromolecule and as a polyelectrolyte should be considered; CMC exerts the following effects on the diffusing salt:

1. As a polyelectrolyte, CMC ionizes in solution to give Na<sup>+</sup> and negatively charged polymer ion. Interionic attraction takes place between the diffusing salt ions and the polymer ions with a consequent decrease in the activity of the diffusing salt and its chemical potential;<sup>8</sup> this gives rise to a decrease in the salt diffusivity.

2. The presence of CMC in solution increases the viscosity with a consequent decrease in salt diffusivity. The ability of CMC to increase solution viscosity depends on the degree of stretching of the polymer molecules; a

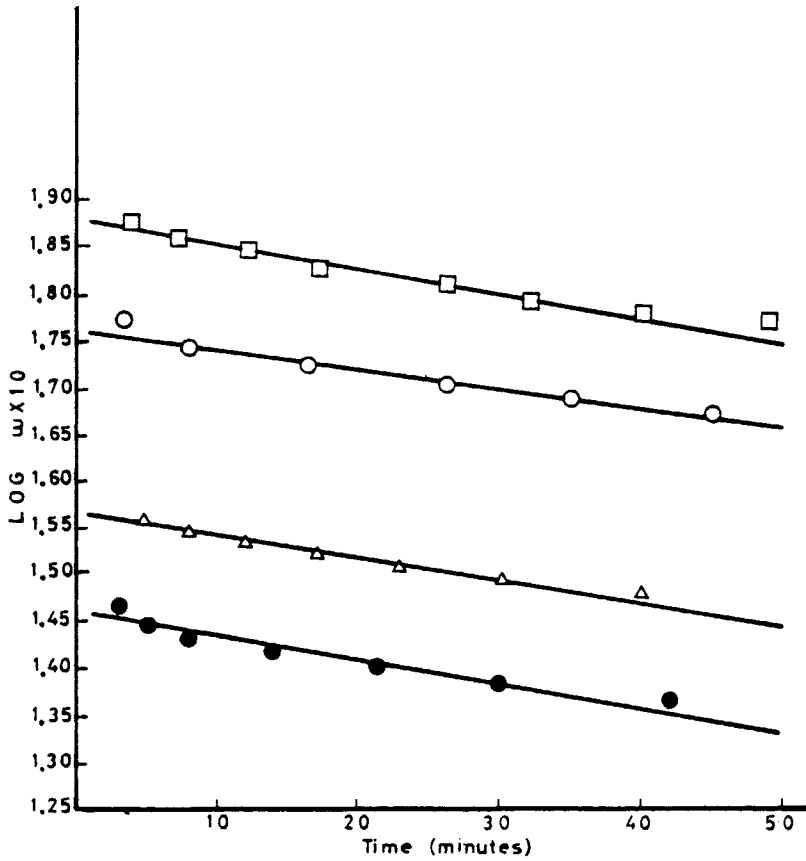


Fig. 1. Log  $\omega$  vs. time for the diffusion of 4.8M NaCl at 25°C. CMC concn (g/L): (●) 2; (○) 4; (Δ) 6; (□) 8.

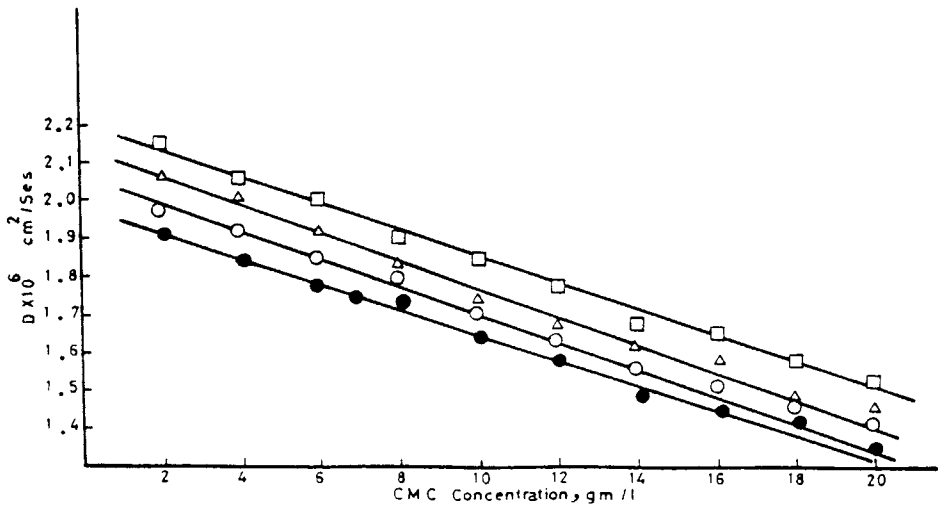


Fig. 2. Effect of CMC concentration on the diffusivity of sodium chloride at 25°C. Sodium chloride concn (M/L): (●) 1.2; (○) 2.4; (Δ) 3.6; (□) 8.

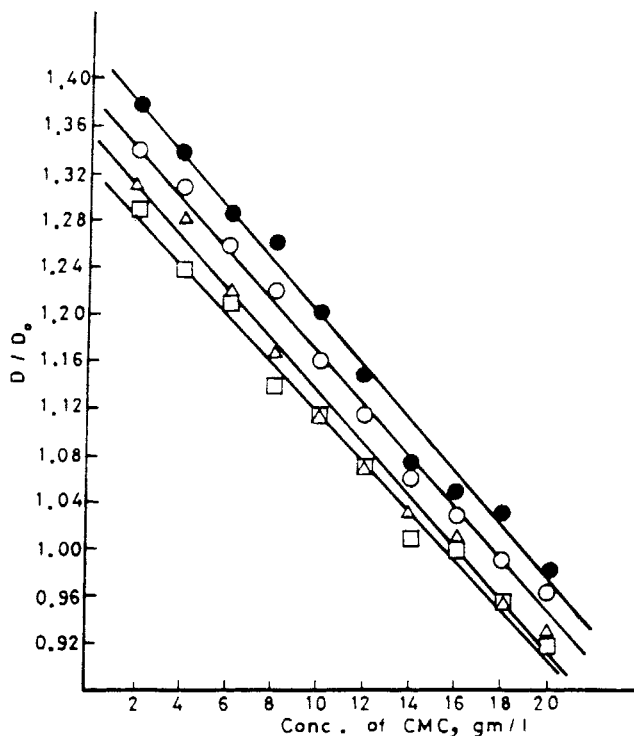


Fig. 3. Effect of CMC concentration on the diffusivity ratio sodium chloride at 25°C. Sodium chloride concn ( $M/L$ ): (●) 1.2; (○) 2.4; (△) 3.6; (□) 4.8.

highly stretched polymer molecule leads to a large increase in solution viscosity while coiled molecules increase solution viscosity to a lesser extent.<sup>9</sup> The degree of polymer stretching depends on the ionic strength of the solution, i.e., CMC concentration and salt concentration, the higher the ionic strength, the lower the ability of the negative segments of the polymer molecule to repel each other to produce a stretched molecule.

3. CMC molecules are bulky and therefore exercise an obstruction effect on the diffusing salt ions. According to Wang,<sup>10</sup> the diffusing species has to get around the polymer molecule, i.e., the diffusion path is prolonged in polymer solutions with a consequent delay in the rate of salt diffusion.

4. CMC is highly solvated polymer,<sup>12</sup> i.e., a large amount of water is removed from the medium to solvate the polar groups existing in the polymer chain and the counter  $Na^+$ . The removal of this enormous amount of free water from the medium decreases the amount of free water available as a solvent; accordingly, the apparent concentration of the diffusing salt would increase with a consequent increase in the chemical potential of the salt and its diffusivity. The present results as shown in Figures 2 and 3 show that the fourth effect (hydration of CMC molecules) predominates at relatively low CMC concentrations where salt diffusivity is higher than that in water. The magnitude of the three retarding effects increases with increasing CMC concentration, where the salt diffusivity decreases to a value below that in water.

For the diffusion of the electrolytes in water, effects 1 and 4 can be quantitatively estimated from the theory of electrolytic diffusion;<sup>1,2</sup> in the

presence of polymer molecules this is not possible because of the lack of some physical parameters pertinent to the polymer molecules such as degree of CMC dissociation, ionic size, and hydration number. In principle, the Robinson–Stokes equations which predicts the diffusion behavior of electrolytes in concentrated solutions can be extended to the case of diffusion of electrolytes in polyelectrolytes. To this end, much work should be done on the determination of the polymer physical parameters mentioned above; besides, a term should be included in the equation to account for Wang obstruction effect and polyelectrolyte viscosity effect.

Figure 2 shows that salt diffusivity can be related to polymer concentration by the equation

$$D = a - bC_p \quad (2)$$

In the light of the theory of electrolyte diffusion it seems that the constant  $a$  in eq. (2), which depends on salt concentration, embodies the salt physical parameters which affect the intrinsic attraction such as ionic size, hydration number, and charge density. The constant  $b$  embodies polymer physical parameters such as degree of dissociation, molecular size, hydration number, and charge density. Astarita et al.<sup>12</sup> studied the diffusion of some nonionic solutes, e.g., allyl alcohol, ethanol, and glycerol in CMC solutions found that the presence of CMC in the medium increases the diffusivity of the solute to a value higher than that in water; this agrees with the present finding. Also Farag et al.<sup>13</sup> who studied the diffusion of dyes in CMC solutions, reported an increase in the diffusivity of the dye molecules in the presence of CMC molecules. Hansford and Litt,<sup>14</sup> who studied the diffusion of benzoic acid in CMC solution, reported a decrease in the diffusivity of benzoic acid in CMC solution. This is probably because Hansford and Litt used relatively concentrated non-Newtonian solutions, where the enhancing effect of polymer solvation is overshadowed by the retarding effects of the polymer molecules, namely, obstruction, viscosity increase, and interionic attraction. Figure 4 shows the effect of CMC concentration on the Einstein–Stokes ratio, the value of the ratio is not constant, but increases with increasing CMC concentration. This confirms the fact that, in polymer solutions, viscosity is not the sole factor affecting the rate of diffusion. Hoshino and Sato,<sup>15</sup> who studied the diffusion of sodium chloride in nonionic polymers such as poly(vinyl alcohol) and poly(vinyl pyrrolidone) found that the salt diffusivity is independent of the macroscopic viscosity, i.e. the Stokes–Einstein ratio was not constant at different macroscopic viscosities. This led the authors to believe that the Stokes–Einstein ratio should be expressed in terms of the microscopic viscosity rather than the macroscopic viscosity. Figure 5 shows the effect of the temperature on the diffusivity of NaCl in CMC; the data fit the Arrhenius equation

$$D = Ae^{-E/RT}$$

with an activation energy of diffusion 2230 cal/mol. Farag et al.<sup>13</sup> who studied the diffusion of dyes in CMC solution, obtained an activation energy

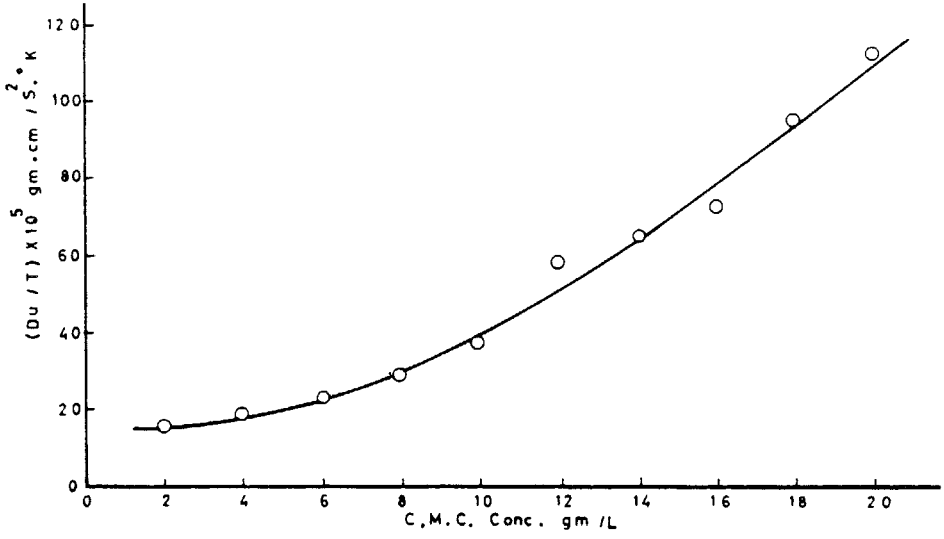


Fig. 4. Einstein-Stokes ratio as a function of CMC concentration at 25°C; sodium chloride concn = 4.8M.

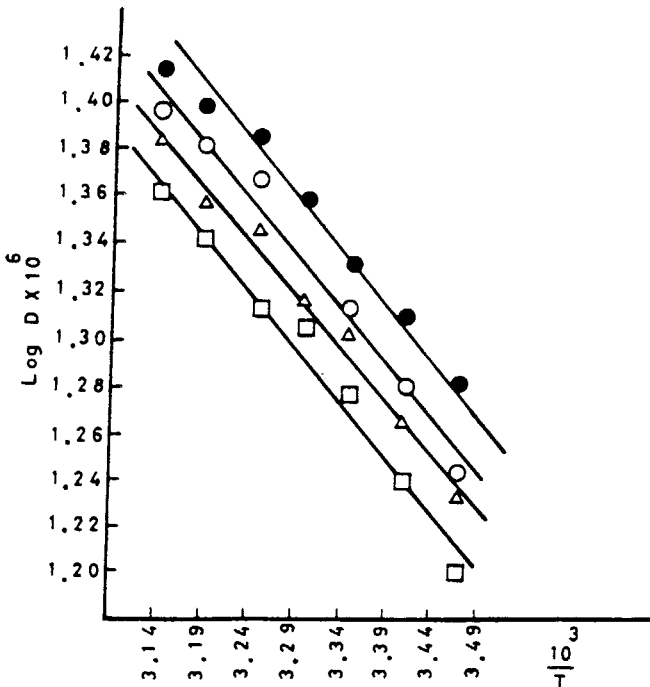


Fig. 5. Log D vs. 1/T for the diffusion of sodium chloride (concn = 4.8M/L) in CMC solutions. CMC concn (g/L): (●) 2; (○) 4; (△) 6; (□) 8.

of 5000 cal/mol; the discrepancy between the value and the present value may be attributed to the fact that Farag et al. used a bulky organic molecule while the present work uses a simple salt.

### APPENDIX: NOMENCLATURE

$a, A, b$	constants
$C_p$	polymer concentration
$D_0$	diffusivity of sodium chloride in water
$D$	diffusivity of sodium chloride in polymer solution
$E$	activation energy for diffusion
$K$	frit constant
$R$	gas constant
$T$	absolute temperature
$u$	viscosity of solution

### References

1. R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, Butterworths, London, 1955.
2. L. Onsager and R. M. Fous, *J. Phys. Chem.*, **36**, 2689 (1932).
3. H. R. Osmer and A. B. Metzner, *Ind. Eng. Chem. (F)*, **11**, 161 (1971).
4. S. U. Li and J. L. Gainer, *Ind. Eng. Chem. (F)*, **7**, 433 (1968).
5. R. M. Navari, J. L. Gainer, and K. R. Hall, *AIChE J.*, **17**, 1028 (1971).
6. F. T. Wall, P. F. Grieger, and C. W. Childers, *J. Am. Chem. Soc.*, **74**, 3562 (1952).
7. F. T. Wall and C. W. Childers, *J. Am. Chem. Soc.*, **75**, 3550 (1953).
8. S. W. Tuwiner, *Diffusion and Membrane Technology*, Reinhold, New York, 1962.
9. T. Kurucsev, *Rev. Pure Appl. Chem.*, **14**, 147 (1964).
10. H. J. Wang, *J. Amer. Chem. Soc.*, **76**, 4755 (1954).
11. S. Lifson and J. L. Jackson, *J. Chem. Phys.*, **36**, 2410 (1962).
12. G. Astarita, H. R. Osmer, and A. B. Metzner, University of Delaware, Newark, DE, unpublished data, 1966.
13. A. A. Farag, H. A. Farag, G. H. Sedahmed, and A. F. El-Nagawy, *J. Appl. Polym. Sci.*, **20**, 3247 (1976).
14. G. S. Hansford and M. Litt, paper presented at Am. Inst. Chem. Eng. Meeting, New York, 1967.
15. S. Hoshino and K. Sato, *Chem. Eng. J.*, **31**, 961 (1967).

Received July 3, 1986

Accepted November 17, 1986