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Diffusion Coefficients of Electrolyte Solutions in Polymers

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An open-ended conductimetric cell has been used to determine mutual differential diffusion coefficients of electrolytes swelling in polymers. We measured diffusion coefficients of KCl and NaCl in aqueous solution, in polyurethane foam, polyvinylalcohol and polyhydroxybutyrate, POxB, commercially labelled as "Biopol."

KEY WORDS Diffusion, polymers, electrolytes, diffusion coefficients

1. INTRODUCTION

Whenever we have an amount of matter, the phenomenon of diffusion is taking place, that is matter is diffusing into matter. Being so widespread and important, the scientific literature has abundant references to diffusion, but the quantitative aspects of very well defined conditions of the different diffusion phenomenon still require a lot of effort to be accurately known. Such is due to the difficulty of setting up experimental conditions appropriate to accurately measure parameters with a well defined physico-chemical meaning. In fact, the movement of matter only due to concentration gradients is very slow compared with mixing (that is the movement of matter due to external forces such as gradients of temperature, vibrations, adsorption phenomena, etc.). Also, it is not easy to set up frames of reference to which the movement of matter is considered in ways which allow accurate measurement.

These factors have frequently been neglected by researchers dealing with diffusion and this consequently affects the information cited in the literature. Furthermore, we often find that the literature does not clearly specify which type of diffusion is under consideration, leading the reader to imagine the wrong scientific framework. For example, there is quite often confusion between mutual molecular isothermal diffusion, thermal diffusion, ionic self-diffusion, tracer diffusion, intradiffusion and interdiffusion.

In the present case, we are interested in the phenomenon of mutual molecular isothermal diffusion of an electrolyte, e.g. KCl, in aqueous solution when this solution is permeating the structure of a polymer. Obviously, this is different from the case of the electrolyte diffusing in aqueous solution contained in a normal vessel.

Let us consider a capillary tube of length a filled with a 0.125 M KCl solution

diffusing into a bulk solution 0.100 M KCl. If we consider that at the mouth of the capillary, that is the plane at $x = 0$, the concentration is always 0.100 M during the diffusion process (an appropriate method of stirring the solution tries to guarantee that), and that the frame of reference to which the movement of the KCl "entities" is that plane at $x = 0$ (appropriate precautions are taken, so that it will be fixed relative to the laboratory coordinates), then, we may consider that the diffusion path is exactly a . Now, we insert a polymer inside the capillary and create conditions so that the 0.125 KCl solution is homogeneously distributed throughout the polymer. We let the KCl diffuse into the bulk solution, but now the diffusing path is in principle much longer than a . However, we cannot measure it and because we are interested in quantifying diffusion in this kind of experimental condition, we will take the diffusion path as being a and therefore the parameter D thus calculated from Fick's 2nd Law is obviously smaller. This parameter may not have a precise physico-chemical meaning, but certainly is useful for practical purposes, if the conditions of its measurement are explicitly indicated so as to be properly understood by the reader.

This case of mutual isothermal diffusion coefficient of a mutual molecular species (salt diffusion as sometimes referred) should not be confused with self-diffusion, tracer diffusion, etc. We should bear in mind that the K^+ has to move with the same speed as the Cl^- , because we have to keep electroneutrality of the solution and that the driving force for this is the concentration gradient.

Diffusion coefficients in the conditions defined above have not yet been reported in the literature. However, there are many references to the phenomenon of diffusion in other conditions, involving polymers.

2. EXPERIMENTAL, RESULTS AND DISCUSSION

Figure 1 shows the experimental apparatus used. It is an extension of our previous method for measuring diffusion¹ (Gold Medal at the Geneva Exhibition of Inventions). In this case we insert a polymer into the capillary so that the diffusion of the electrolyte has now to follow along the tortuous path of the polymer structure. However, in the solution of the diffusion equation from Fick's 2nd Law discussed in our previous papers,² we take a as being the physical length of the glass capillary. Naturally this is because we are interested in quantifying the diffusion of an electrolyte in a solution contained in a fixed amount of a specific polymer.

A number of tests were made to ensure reproducibility of the technique, that is, that the polymer is inserted always in the same conditions in every experiment, and that these conditions reproduce the practical situation of the polymer imbibed with an electrolyte solution.

Table I presents the results. They show a D lower than what we have measured in "free diffusion" (e.g., 1.938 and $1.845 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for 0.01 M and 0.1 M KCl respectively) but we were surprised that it is not much lower, as we expected once the diffusion path should be much larger.

Our interpretation is that the ions move so much in contact with the polymer surface that it plays some sort of a role in accelerating their movement down the concentration gradient.

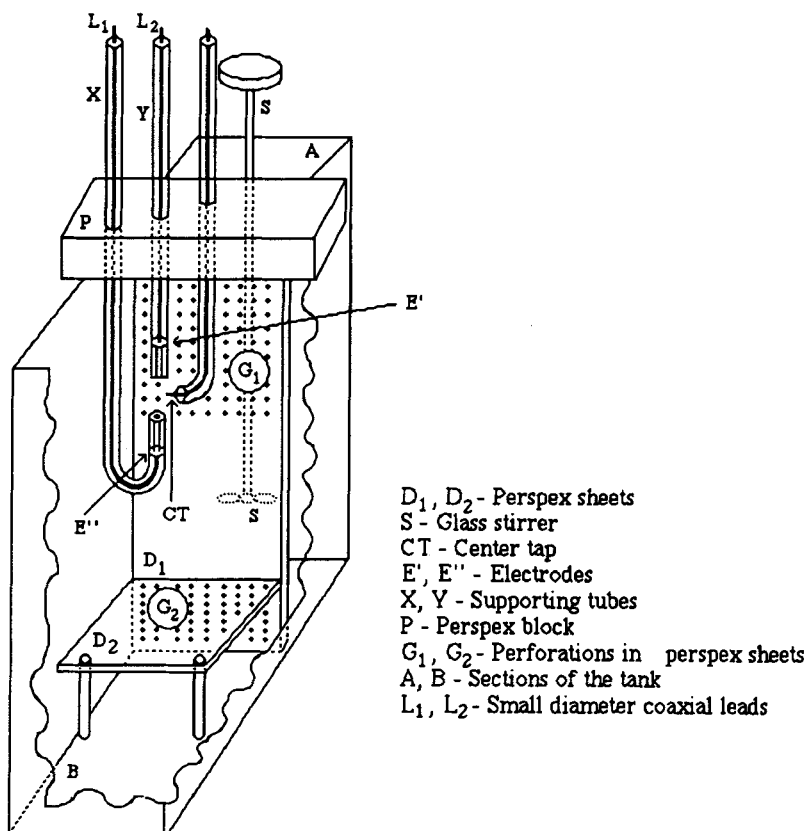


FIGURE 1 Illustration of the cell showing location of capillaries and centre tap electrode, and arrangements for circulation of solution.

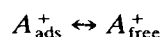
TABLE I

Diffusion coefficients of KCl and NaCl solutions in polyurethane, PVA and POxB

Polymer	Electrolyte	Conc. / mol dm ⁻³	D _{obs} / 10 ⁻⁹ m ² s ⁻¹	σ _{n-1}
polyurethane	KCl	0.01000	0.6202	0.162
		0.1000	0.5370	0.0764
polyurethane	NaCl	0.01000	0.7039	0.224
		0.1000	0.5979	0.222
PVA	KCl	0.1000	1.282	0.132
POxB	KCl	0.1000	0.4297	0.0555

In "free diffusion" the "Brownian movements" are equal in all directions. If there is a net flow of matter from an elemental cube of volume dv at concentration c to an adjacent elemental cube of volume dv' at a smaller concentration c' is because there will be more particles going from dv to dv' than the reverse. But, obviously, this net flow of matter from dv to dv' is very slow. The walls of the container are too far away to play a significant role, even in a glass capillary 2.5 mm in diameter as is our previous case.

Now in the polymer, its surface may play a significant role. Interaction with the walls is now significant because any ion is close to them. Polymer-solvent and polymer-solute interactions are certainly strong and may be such that the end result is to speed up the flow of matter from an elemental cube of volume dv to the adjacent dv' down the gradient concentration. An equilibrium is established between adsorbed ionic species A_{ads}^+ and A_{free}^+



As the surface down the concentration gradient is freer from A_{ads}^+ , this equilibrium may rapidly move \rightarrow in volume dv and rapidly move \leftarrow in the adjacent dv' so that the net movement of A^+ down the wall is much faster than in similar conditions in free diffusion.

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