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Ionic Diffusion in Polymers

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Summary: Scleroglucan aqueous solutions and gels were selected to study the dependence of diffusion behavior of alkali and alkaline-earth metal ions on matrix structural characteristics. Stokes and free diffusion experimental methods for obtaining diffusion coefficients were contrasted. Three different behaviors. corresponding to three well-defined concentration regimes of the polymeric system were found.

Keywords: hydrophilic polymers; ionic diffusion; matrix transport properties; polysaccharides; scleroglucan

Introduction

Transport properties in macromolecular systems have applications in a wide variety of industrial fields ranging from controlled drug delivery or diffusion-controlled kinetic chemical processes[1] to Enhanced Oil Recovery [2,3]. To design technological devices, it is necessary to have an understanding of the diffusant transport properties in a given matrix (polymer-solvent) which are influenced by changes in structural characteristics [4].

This work presents a systematic study of ionic diffusion through scleroglucan aqueous systems.

Scleroglucan is an exocellular β-(1,3)-glucan excreted by the fungus of the genre Sclerotium. Its primary structure has been characterized as a lineal chain of β-(1,3)-D-glucopiranosil units with a lateral branch of a β-(1,6)-D-glucopiranosil unit every three units of the main chain [5] (Figure 1).

In aqueous solutions, inter and intra-macromolecular hydrogen bonds generate cluster structures with variable persistence-length and rigidity [6].

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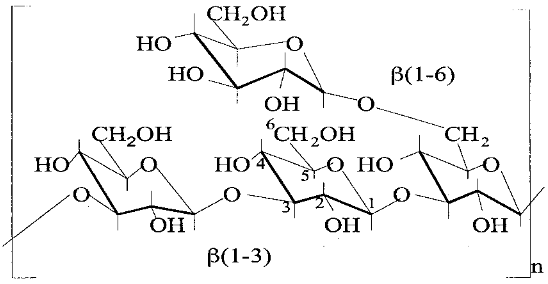

Figure 1. Scleroglucan monomer unit.

Experimental

Diffusion behavior of ions with different charge, mass and size in a matrix with variable scleroglucan concentration was studied.

We chose soluble and neutral salts: nitrates of alkali and alkaline-earth metals. These cations present increasing radius size.

The effective diffusion coefficients were determined, at (25±1) °C, by two methods: 1) Stokes, and 2) free diffusion [7]. Results were contrasted; those of the free diffusion method resulted were more reproducible.

Concentration regimes for scleroglucan systems have transition ranges with the following central values [7].

Diluted regime < 0.15%w/w < semi-diluted regime < 0.6%w/w < concentrated regime or gels

The diffusion behavior depends on the polymer concentration, in agreement with structural changes observed on the matrix (Figure 2).

In the diluted regime diffusion coefficients initially decrease exponentially when concentration increases (except for LiNO3): the small ions undergo a hydrodynamic obstruction effect [9]. A linear correlation between this exponential behavior and ionic hydrodynamic radii is observed.

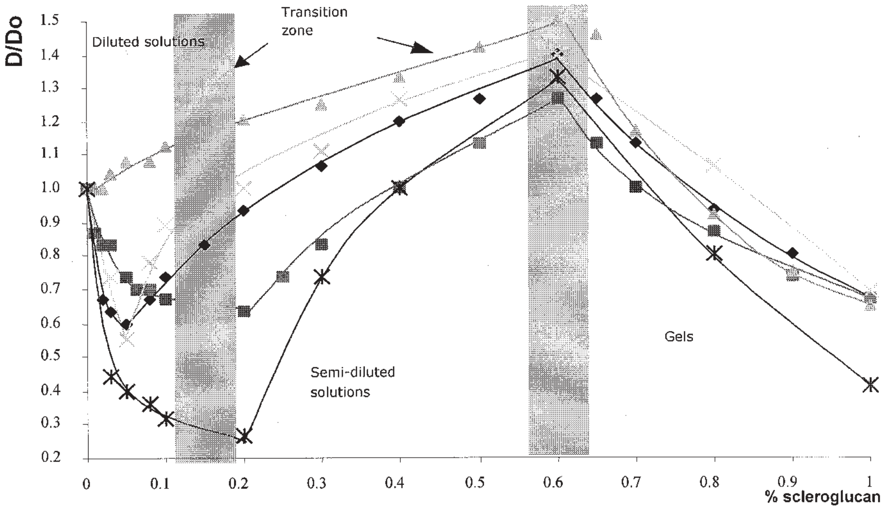

Figure 2. Diffusion of salts in scleroglucan aqueous solutions (D) relative to water diffusion (D_0): (♦) $NaNO_3$; (■) KNO_3; (▲) $LiNO_3$; (X) $Mg(NO_3)_2$; (*) $Ba(NO_3)_2$.

In the semi-diluted regime, the diffusion coefficients increase with scleroglucan concentration. In this range, clusters of increasing size are formed whereas their number decreases, as determined by Scanning Electronic Microscopy [8]. The possibility of self-generated ionic channels in a dynamic process could explain the higher diffusion coefficients obtained in this region [8,10].

In concentrated regime (gel), diffusion coefficients also show an exponential decrease with polymer concentration as found in others systems [11-13]. The diffusion behavior observed in this work can be explained taking into account the size and charge of the ions and the increasing tortuosity of the matrix [14].

Conclusion

It has been shown that the transport through these systems is affected by the structural characteristics of the system because changes in the diffusion behavior of solutes coincide with the concentration regimes of the matrix.

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