Self-diffusion of the Sulfate Ion in Gelatin Gels

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The self-diffusion of ions in gels has not been studied so extensively as in aqueous solutions. In general, the diffusion process in gels is made more complicated than in liquid systems by such factors as the geometry of the diffusion path and the adsorption of the ion by the gel substance. Clearly these factors are closely related to the structure of gels. It is expected that the study of the self-diffusion of ions will give us useful information about the structure of gels as well as the nature of the transport phenomena in gels. In this paper the self-diffusion of the sulfate ion in gelatin gels will be investigated.

Experimental

The gelatin used in the present experiment was Merck's reagent for chemical use. In order to minimize its salt content, the aqueous solution (sol) of the gelatin was passed through an ion-exchange column. After that the salt content was found to be 0.3%. ^{35}S labeled sodium sulfate was obtained from the Radiochemical Center, England, as a carrier-free material. It was isotopically diluted to a proper concentration and purified by recrystallization.

For the measurement of diffusion, the layer analysis method was used. The diffusion cell was almost identical with that of Nachtrieb and Petit[1],

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1) N. H. Nachtrieb and J. Petit, *J. Chem. Phys.*, **24**, 746 (1956).

although some details were modified. The cell was made up of six disks (denoted from the top as disk No. 1 to disk No. 6) of poly(methyl methacrylate) Each disk, 40 mm. in diameter and 5 mm. in thickness, could be rotated around a common vertical axis. Disks No. 2 to No. 5 bore holes 5 mm. in diameter at a point 1 cm. from the center. They were aligned by means of a locating pin so that they formed a straight diffusion column. The two ends of the diffusion column were covered by disks No. 1 and No. 6, which bore no holes.

The gelatin sol, which contained inactive sodium sulfate of a known concentration, was poured into the holes of disks No. 3 to No. 5, which had been aligned. The same sol also containing radioactive sodium sulfate of the same concentration as above was poured into the hole of disk No. 2. They were then left to stand in a constant temperature bath. After complete gelation, the two gel blocks were placed in contact with each other by rotating the disks and by aligning the holes by the locating pin, as has been stated above. This time of contact was taken as time zero for diffusion. After an appropriate time (usually, 4 to 5 hr.), the cell was taken out of the bath and each disk was rotated with respect to its neighbor in order to shear the column of gel into four sections. The radioactivity of the sodium sulfate in each section (C) was measured after it had been mounted on a porcelain dish as a uniform film. The self-absorption correction was not made, since each disk contained exactly the same amount of gelatin and we needed only the relative intensity of radioactivity with respect to the initial one in disk No. 2 (C_0). The self-diffusion coefficient of the sulfate ion was thus calculated from the observed value of C/C_0 with the aid of the Stefan-Kawalki Tables[2].

The temperature of most of the diffusion, experiment was 25°C. For the measurement of the activation energy for self-diffusion, the temperature ranged from 10 to 28°C with 11% gelatin gel containing sodium sulfate of 0.001 mol./l.

Results and Discussion

In Fig. 1 the self-diffusion coefficient of the sulfate ion in gelatin gels, D_g, at 25°C is plotted against the square root of the concentration of sodium sulfate in the gel. Each value of the diffusion coefficient is a mean of three separate runs. The standard deviation was less than 3%. For the sake of comparison, the self-diffusion coefficient of the sulfate ion in aqueous solutions at 25°C, D_w, as measured by Nielsen et al.[3], is also shown in Fig. 1.

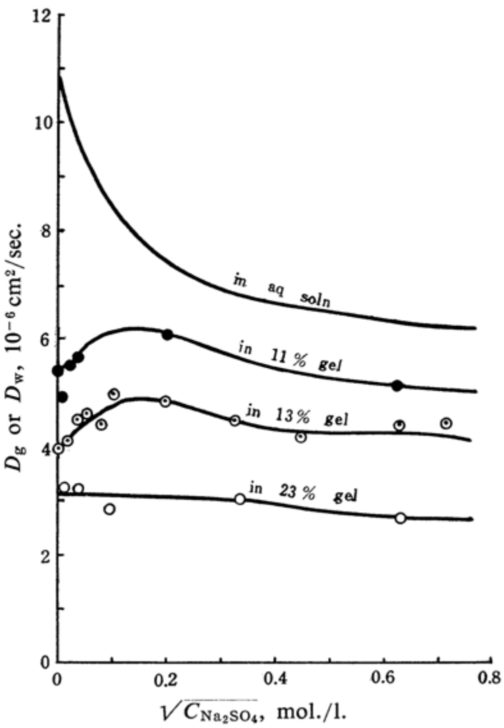

Fig. 1. Self-diffusion coefficient of sulfate ion vs. square root of concentration of Na_2SO_4 in gelatin gels (D_g) and in aqueous solutions (D_w) at 25°C.

It may be seen from Fig. 1 that the D_g value in 11% gel is about half as large as D_w when the concentration of sodium sulfate is very low, but at higher concentrations of sodium sulfate the two values approach each other. As the gel concentration increases, the D_g value decreases; also, the dependence of the D_g value on the concentration of sodium sulfate becomes smaller. The initial linear decrease of the D_w value with respect to the square root of the concentration of sodium sulfate in aqueous solutions may be explained in terms of the Onsager theory of ionic diffusion[4,5]. This behavior is quite different in gels, where the D_g initially increases a little but decreases slightly as the concentration of sodium sulfate increases further. In 23% gel, no initial increase in the D_g is observed.

It has reasonably been assumed that the sulfate ion is adsorbed strongly by the gelatin molecule to form intra- or intermolecular cross-linking. Indeed, we found that the "melting point" of gelatin gel[6] increases as the addition of sodium sulfate increases. The activation energy for the self-diffusion of the sulfate ion in 11% gel at the sulfate concentration of 0.001 mol./l. was found to be 5.9 kcal./mol. This value is of the same order of magnitude as that for the self-diffusion of ions in ion-exchange resins[7]. It is to be concluded, therefore, that the self-diffusion of the sulfate

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ion in gelatin gels proceeds via the exchange of the adsorbed ion. Of course, the geometry of the diffusion path plays an important role in the diffusion of the adsorbed ion, since the self-diffusion coefficient decreases appreciably as the concentration of gel increases.

Bloksma[8] measured the self-diffusion of sodium and iodide ions and of urea in clay pastes. He separated two labyrinth factors, geometry and adsorption, and proposed to determine them. It is, however, not easy to determine each factor separately unless some assumptions are made. Probably the combined effects are responsible for the curious dependence of the D_g value on the concentration of sodium sulfate.

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