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Diffusional Behaviour of $H_2{}^{32}PO_4^-$ and $^{131}I^-$ ions in Agar Gel

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The tracer-diffusions of $H_2{}^{32}PO_4^-$ and $^{131}I^-$ ions are determined at 25°C in different concentrations of Na_2SO_4 and K_2SO_4 solutions immobilized in 2.5% agar gel. The results are compared with the theoretical values and are explained in the light of their ionic sizes, shape and hydration characteristics. The obstruction effect of gel on tracer-diffusion of both the ions was also studied.

INTRODUCTION

Recent studies on diffusion of a number of ions have been carried out by several workers in aqueous[1, 2] as well as in gel medium[3–5]. In continuation with our previous work, the present paper deals with the measurement of tracer diffusion of $H_2{}^{32}PO_4^-$ and $^{131}I^-$ ions in different concentration of sodium and potassium sulphate solutions (10^{-6}–10^{-1} M) immobilized in 2.5% agar gel at 25°C. Further, the obstruction effect of agar gel on tracer-diffusion of both the ions was studied in 0.01 M potassium sulphate solution at 25°C.

EXPERIMENTAL

Radioactive $H_2{}^{32}PO_4^-$ and $^{131}I^-$ ions, obtained from Bhabha Atomic Research Centre, Bombay, were used as such after appropriate dilution.

The method for setting of the gel and its measurement was reported earlier[4].

RESULT AND DISCUSSION

The experimental and theoretical values of diffusion coefficients are calculated from standard equations[4, 6]. The plots of D *vs.* $\sqrt{C}$ for both the ions in Na_2SO_4 and K_2SO_4 solutions (Fig. 1) shows that the experimental values are higher than those of theoretical values at all concentrations studied, indicating that in 2.5% agar gel, the process of diffusion is faster than in aqueous solution. Further, in case of $H_2{}^{32}PO_4^-$ ions, after 10^{-2} M concentration, an increase in tracer-diffusion was observed whereas in case of $^{131}I^-$ ions, a constant decrease was observed. The different behaviour of these tracer ions at higher concentrations of electrolyte solutions is due to differences in their ionic size, shape and hydration characteristics.

Hydrated iodide[7] and orthophosphate[8] ions have effective diameter of 3 Å and 4.5 Å respectively. Further, $^{131}I^-$ ions are spherical whereas $H_2{}^{32}PO_4^-$ ions are

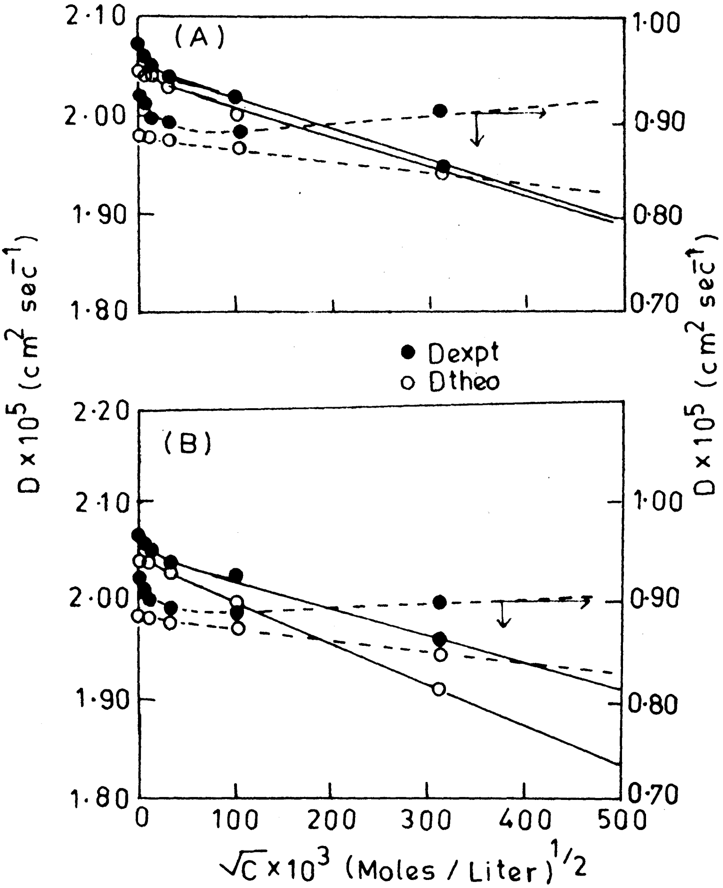

Fig. 1. Concentration dependence of tracer-diffusion of $H_2{}^{32}PO_4^-$ (– – – –) and $^{131}I^-$ (————) ions in (A) Na_2SO_4, and (B) K_2SO_4 solutions immobilized in 2.5% agar gel at 25°C

tetrahedral in structure[9]. Thus, the effective diameters of hydrated iodide and orthophosphate ions have swelled by 39% and 65% respectively of their known diameter. Hence the increase in ionic size on hydration is much greater for orthophosphate ions. Further, the localization of charge on one oxygen in $H_2{}^{32}PO_4^-$ ions (not spherically distributed as in iodide ion) permits greater interaction with water molecules and therefore less mobility. But the charge on anion does not produce stronger solvation[10]. Due to lesser hydration of orthophosphate ions, activation energy for the viscous flow in solution decreases from that for the pure solvent even though the ions itself increase the bulk viscosity of the solution[11]. Whereas $^{131}I^-$ ions which are slightly smaller than $H_2{}^{32}PO_4^-$ ions, orient the water molecules immediately adjacent to ions more firmly, thus increasing the activation energy for viscous flow. Due to weak electric field, larger orthophosphate ions disturb or distort the normal water structure and increase the movement of ions.

Fig. 2 shows decrease in tracer-diffusion coefficient (D_g) of $H_2{}^{32}PO_4^-$ and $^{131}I^-$ ions with agar gel concentration (ω). The decrease in D_g with increasing gel concentration was due to mechanical obstruction offered by macromolecules of the agar gel to the diffusing ions[12]. The irregular network of macromolecules in gel act merely to lengthen the diffusion path and this obstruction effect was described by formation factor F which is given by:

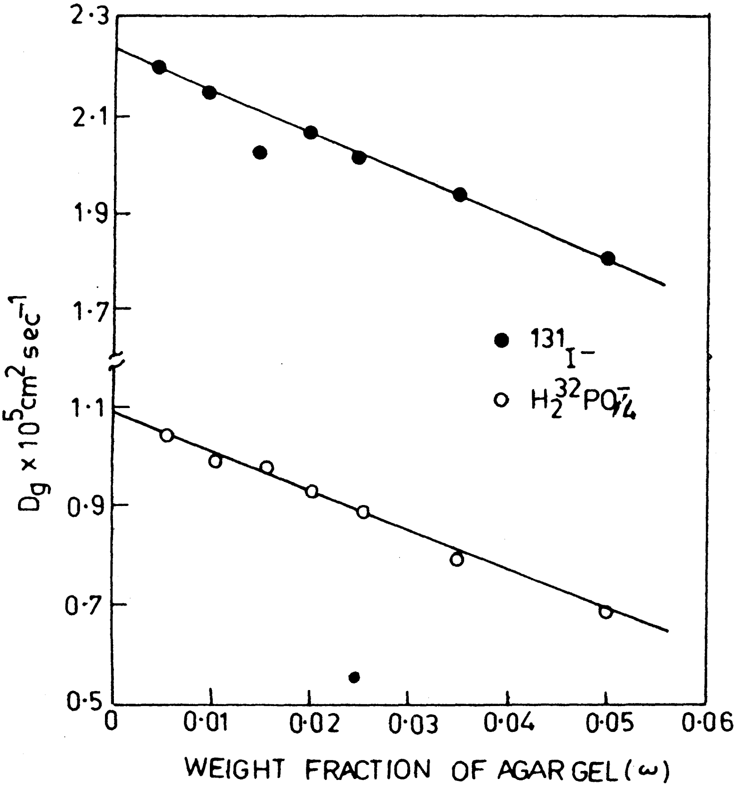

Fig. 2. Variation of tracer-diffusion coefficient of $H_2{}^{32}PO_4^-$ and $^{131}I^-$ ions in 10^{-2} M K_2SO_4 solution immobilized in different weight fractions of agar gel at 25°C

$$\frac{D_s}{D_g} = F \simeq \frac{1}{1 - \alpha\omega} \simeq 1 + \alpha\omega \qquad (1)$$

where α is the slope of the plot D_g *vs.* ω (Fig. 2) divided by D_s which is extrapolated value of tracer-diffusion coefficient to zero agar content. The values of α for labelled orthophosphate and iodide ions were calculated to be 6.12 and 4.26 respectively whereas theoretical value of α is 0.42, calculated merely on the basis of geometry of agar macromolecules[12]

Thus, the gel structure obstructs the motion of the ions. In order to explain the observed discrepancies in experimental and theoretical values, other interactions between ions, water and polymer molecules should be considered. The higher obstruction in the diffusion path is due to hydration of polymer molecules. The hydration values (H) of agar macromolecules in the presence of different ions are calculated by the relation[12].

$$\alpha = \frac{1}{d_a} + \frac{H}{d_w} d_w(\beta - 1) \tag{2}$$

where d_w and d_a are the densities of water (0.997) and agar (1.6) respectively, β is shape factor (=5/3 for needles) and H is the hydration of agar (*i.e.*, grams of bound water per gram of anhydrous agar). Using equation (2), the hydration values (H) were calculated to be 8.56 and 5.76 for $H_2{}^{32}PO_4^-$ and $^{131}I^-$ ions respectively. It was observed that both α and H values of $H_2{}^{32}PO_4^-$ ions were higher than those of $^{131}I^-$ ions which is due to the fact that extent of hydration depends on the charge density of the ion. In comparison to orthophosphate ions, iodide ions have higher charge density; hence these ions will be more hydrated than orthophosphate ions. Thus, in the presence of $^{131}I^-$ ions, fewer water molecules were available for the hydration of agar, giving thereby less obstruction in comparison to $H_2{}^{32}PO_4^-$ ions.

Thus, although diffusion coefficient is found to increase in agar gel in comparison to theoretical values, higher concentration of gel obstructs the path of diffusion.

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