Obstruction Effect & Self-diffusion of Zinc Ion in Agar Gel

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The self-diffusion coefficient of Zn^{2+} ion has been measured in agar gel of different concentrations over the temperature range 25-50° C, keeping the electrolyte concentration constant. The obstruction effect has been calculated in terms of a factor, α, which is given by the slope of the plot of diffusion coefficient (D_g*) versus weight fraction of the agar (ω) divided by the extrapolated value of D_g^* to zero agar content. The factor α is found to be independent of temperature. From the value of α the extent of hydration for anhydrous agar is estimated. The decrease in activation energy and value of D_0^* with increasing gel concentration is explained in the light of transition state theory of diffusion.

AGAR gels had been used by several workers as a stationary phase for the diffusion of electrolytes[1-3] and non-electrolytes[4-6], and a linear dependence of diffusion coefficient on gel concentration had been observed.

In our previous communications[7,8] we reported the effect of gel concentration on the self-diffusion of the chromate ion. The study is now extended to the Zn^{2+} ion in agar gels of different concentrations at different temperatures, keeping the electrolyte concentration at 10^{-5} M. From the results the obstruction effect has been evaluated. The variation of the activation energy for the process with the gel concentration has been also determined.

Materials and Methods

[65]Zn was obtained from the Bhabha Atomic Research Centre, Bombay in the form of $ZnCl_2$ and was used in the same form for studying the diffusion.

The gel concentration was varied from 1.5 to 3% keeping the $ZnCl_2$ concentration at 10^{-5} M and the temperature was varied from 25° to 50°C. The zone-diffusion technique was used for determining the self-diffusion coefficient. Experimental procedure and calculations for obtaining the diffusion coefficient were reported earlier[7].

Results and Discussion

The study covers two aspects, viz. the obstruction effect on the diffusion of ions and the effect of gel concentration on the activation energy.

Variation of self-diffusion coefficient D_g^* of Zn^{2+} ion (10^{-5} M) with the weight fraction of agar (ω) for different temperatures is shown in Fig. 1, each value of D_g^* is the average of four independent experiments with an accuracy of about 0.2%. A decrease in D_g^* with increase in gel concentration is observed which is due to mechanical obstruction of the network of agar. This follows the relation[2],

$$D_g^* = D_s^* * - a\omega \qquad \qquad ...(1)$$

where D_s^* is the extrapolated value of D_g^* to zero agar content for the given concentration of the electrolyte and a is the slope of the plot of D_g^* versus ω. The value of α ($= a/D_s^*$) comes out to be 2.84 which is in agreement with the reported value of 3.1 for the diffusion of Na^+ ion in agar gel[3]. Further, it is to be noted that α is independent of temperature (Fig. 1) indicating that macromolecular geometry obstructing the diffusion of ions remains constant over the temperature range studied. The value of α is related to the formation factor F by the following expression[3],

$$F = \frac{1}{1-\alpha\omega} \simeq 1 + \alpha\omega \qquad \qquad ... (2)$$

Considering the gel as a collection of randomly oriented three-dimensional network of needles, the theoretical value of the formation factor is given by the relation[9],

$$F = 1 + \rho \, (\beta - 1) \qquad \qquad ...(3)$$

where β is a shape factor (5/3 for needles) and ρ is the volume fraction of the gel molecules (ω/d_a), where d_a is the density of agar which is taken to be 1.6. Substituting these values, equation (3) becomes,

$$F = 1 + 0.42 \, \omega \qquad \qquad ...(4)$$

while the experimental results lead to the relation (5),

$$F = 1 + 2.84 \, \omega \qquad \qquad ...(5)$$

The higher experimental value of α suggests that the gel structure is more effective in obstructing the movement of the ions than that predicted by the theory. This large deviation between the experimental and theoretical values of α is thought to be due to extensive hydration of the agar gel which effectively increases the size of its molecules leading to a larger obstruction to the diffusing ions.
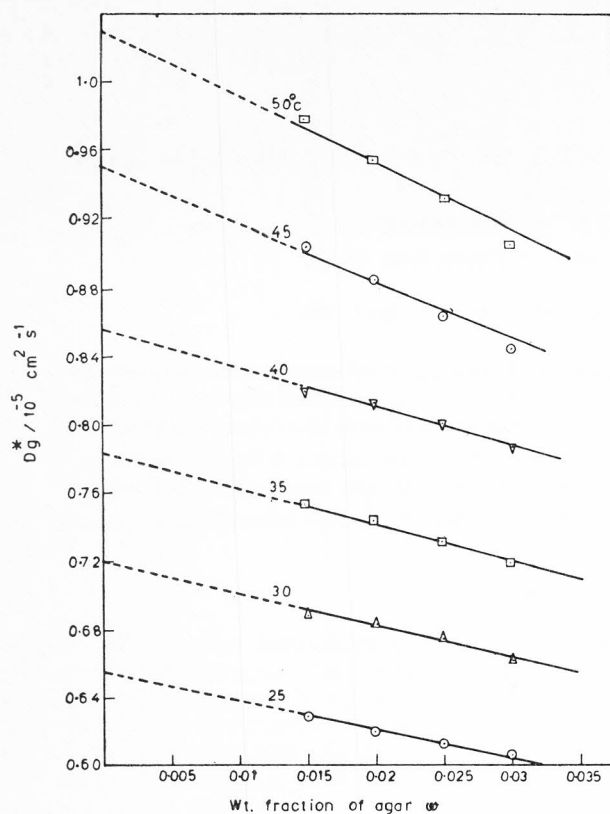
Fig. 1 — Obstruction effect in the self-diffusion of Zn^{2+} in $1 \times 10^{-5} M$ $ZnCl_2$ solution.

Fig. 2 — Variation of (a) D_0^* with $W^{-2/3}$ and (b) E with $W^{1/3}$ for $1 \times 10^{-5} M$ Zn^{2+} ion concentration

TABLE 1 — VARIATION OF D_0^* AND E FOR THE SELF-DIFFUSION OF Zn^{2+} ION WITH GEL CONCENTRATION

[Gel] (%)	$D_0^*/10^{-3}$ cm² s⁻¹	E/kJ mol⁻¹
1.5	1.918 ± 0.152	14.27 ± 0.21
2.0	1.671 ± 0.084	13.95 ± 0.13
2.5	1.33 ± 0.086	13.41 ± 0.17
3.0	1.119 ± 0.074	13.01 ± 0.17

An estimate of hydration of agar can be made by considering the effective volume fraction of gel macromolecules (ρ) which for $\omega \ll 1$ is given by[10] Eq. (6),

$$\rho = \left(\frac{1}{d_a} + \frac{H}{d_w} \right) . d_w. \omega \qquad ...(6)$$

Substituting the value of ρ in Eq. (3) and comparing it with Eq. (2), one arrives at the following expression,

$$\alpha = \left(\frac{1}{d_a} + \frac{H}{d_w} \right) . d_w. (\beta - 1) \qquad ... (7)$$

Using Eqs (7) and (5), the amount of bound water (in grams) per gram of anhydrous agar (H) comes out to be 3.63 which is in reasonable agreement with value of 4.02 calculated from the value of α (3.1) reported by Langdon and Thomas[3].

The variation of the diffusion coefficient of Zn^{2+} (1×10^{-5} M) has been studied for different gel concentrations at several temperatures. The variation of diffusion coefficient (D_g^*) of Zn^{2+} ($1 \times 10^{-5}M$) with temperature has been examined by least-squares fitting (Table 1) the diffusion coefficient data to the Arrhenius equation,

$$D_g^* = D_0^* \ e^{-E/RT} \qquad ...(8)$$

for each of the gel concentrations studied. Both D_g^* and E decrease with increasing gel concentration. These observations can be explained by correlating the Arrhenius equation with that of Eyring[11] for the self-diffusion of an ion. This leads to Eq. 9,
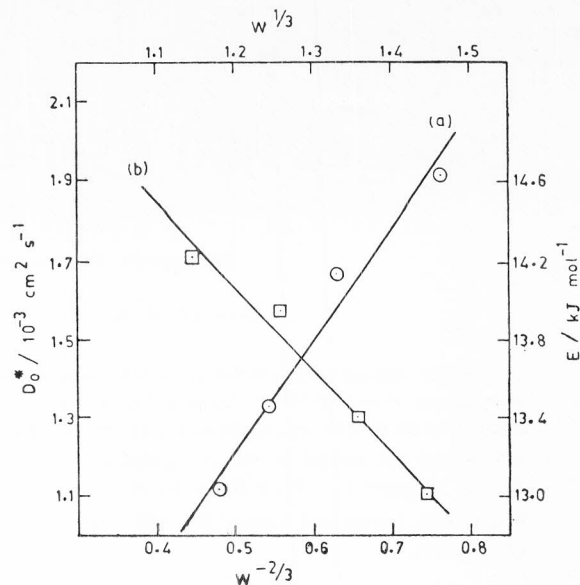
$$D_0 = e\lambda^2 \ \frac{kT}{h} \ e^{\triangle S\ddagger/R} \qquad ...(9)$$

Assuming the entropy of activation to be independent of the agar content, the decrease in D_0^* implies that λ should also decrease with gel concentration. Assuming $\triangle S\ddagger$ to be constant in the range of the gel concentration studied, the transition state theory predicts that λ should vary with $W^{-1/3}$ and hence D_0^* with $W^{-2/3}$ where W is the weight percentage of agar. This is borne out by the linear relationship observed in the plot of D_0^* and $W^{-2/3}$ (Fig. 2). The activation energy is also likewise smaller for the more concentrated gels and as is seen from Fig. 2, E is a linear function of $W^{1/3}$. As the concentration of gel increases, the macromolecules of agar appear to limit the elementary jumps to only shorter distances resulting in the lowering of activation energy as observed.

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