Effect of Electric Field on Tracer-diffusion of $H_2{}^{32}PO_4^-$ Ions in Agar Gel

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In continuation of the previous work[1], the present work reports the effect of d.c. field on tracer-diffusion of $H_2{}^{32}PO_4^-$ ions in 2.5% agar gel containing sodium nitrate, potassium nitrate, sodium sulphate and potassium sulphate solutions (0.001 M) at 25°. Further, the effect of intensity and duration of d.c. field on tracer-diffusion on $H_2{}^{32}PO_4^-$ ions has been studied.

Results and Discussion

In the absence of electric field, a Gaussion distribution of $H_2{}^{32}PO_4^-$ ions was obtained which gives a single value of tracer-diffusion coefficient[2]. But in the presence of d.c. field, the migrated central zone spreads unequally on both sides giving asymmetric Gaussion distribution (Fig. 1). Thus
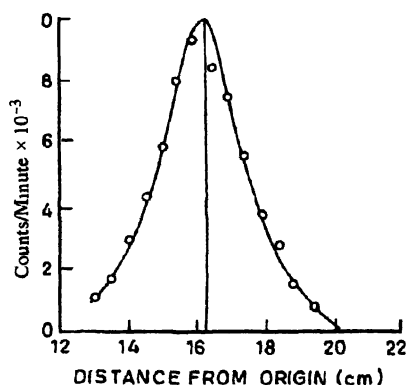

Fig 1 Plot of activity (counts/min) of $H_2{}^{32}PO_4$ ions vs distance from origin in 10^{-3} M Na$_2$SO$_4$ solution immobilised in 2 5% agar gel at 25° under d.c field of 4 615 V cm^{-1} for 4 h.

a plot of log a vs x^2 gives two lines, the slopes of which give two unequal values of electrodiffusion coefficients D_1 and D_2 in and against the field direction (Fig. 2). Under similar conditions of temperature and concentration, both the values of D_1 and D_2 are greater than simple tracer-diffusion (D_0), i.e. in the absence of electric field (Table 1).

With increase in intensity and duration of field, electrodiffusion coefficients of $H_2{}^{32}PO_4^-$ ions increase due to increase of ionic mobilities with field intensity. The two unequal values of electrodiffusion coefficient can be explained by the fact that in ordinary diffusion, both the partner ions move with a common speed so that there is no charge sepa-
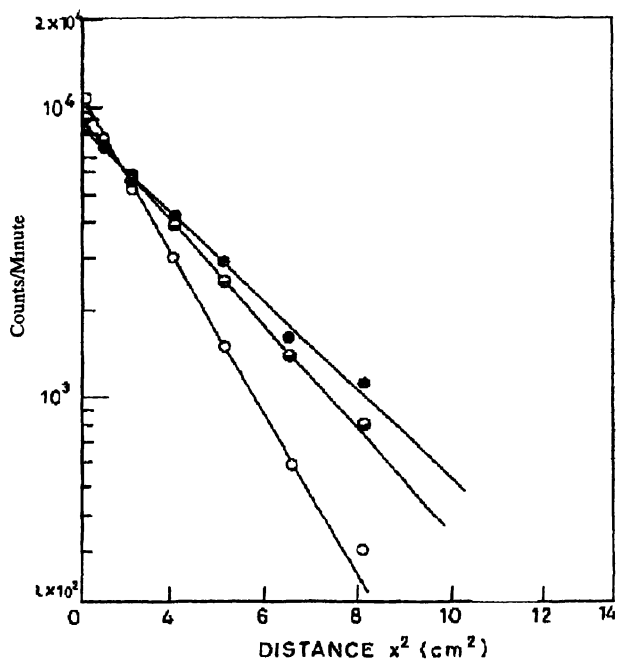

Fig. 2. Plots of log of activity a (counts/min) of $H_2{}^{32}PO_4$ ions vs square of distance in 10^{-3} M Na$_2$SO$_4$ solution immobilised in 2 5% agar gel at 25° under d.c field of 4.615 V cm^{-1} for 4 h . (O) D_0 in the absence of field, (⊖) D_1 in the field direction and (●) D_2 against the field direction

ration. But in electrodiffusion, the two ions diffuse in opposite directions with their characteristic mobilities which are proportional to their tracer-diffusion coefficients This results in a charge separation which lasts till the formation of new ion-atmosphere at these sites. During this relaxation period, an intense electric field due to charge separation acts in opposite direction to the applied field. This is effective upto a distance of molecular dimensions. This reverse field would favour larger Brownian displacement in the opposite direction. The integrated effect of this over a finite period gives rise to asymmetry in Brownian displacement in the two directions as observed in the present study.

Further, in and against the field direction, there is small but finite difference between the size of ion-atmosphere and/or the relaxation time of the diffusion ion in occupy-

TABLE 1—TRACER-DIFFUSION COEFFICIENTS OF $H_2{}^{32}PO_4$ IONS IN DIFFERENT ELECTROLYTES (0.001 M) IMMOBILISED IN 2.5% AGAR GEL AT 25° IN PRESENCE OF D.C. FIELD

Electrolyte (0.001 M)	Field applied V cm^{-1}	$D \times 10^5$ cm^2 s^{-1}	Period (h)		
			2	3	4
NaNO$_3$		D_0	0.906	0.906	0.906
	2.307	D_1	1.002	1.227	1.475
	2.307	D_2	1.208	1.354	1.766
		D_0	0.906	0.906	0.906
	4.615	D_1	1.042	1.209	1.640
	4.615	D_2	1.298	1.529	2.002
KNO$_3$		D_0	0.913	0.913	0.913
	2.307	D_1	1.011	1.292	1.594
	2.307	D_2	1.239	1.414	1.785
		D_0	0.913	0.913	0.913
	4.615	D_1	1.092	1.292	1.765
	4.615	D_2	1.435	1.664	2.018
Na$_2$SO$_4$		D_0	0.902	0.902	0.902
	2.307	D_1	0.927	1.119	1.377
	2.307	D_2	1.161	1.445	1.626
		D_0	0.902	0.902	0.902
	4.615	D_1	1.171	1.292	1.579
	4.615	D_2	1.441	1.549	2.015
K$_2$SO$_4$		D_0	1.122	1.122	1.122
	2.307	D_1	1.029	1.107	1.723
	2.307	D_2	1.284	1.805	2.208
		D_0	1.122	1.122	1.122
	4.615	D_1	1.960	2.052	2.765
	4.615	D_2	2.590	3.079	4.033

ing holes in and against the field direction. This is valid for each jump of the ions. This results in the difference between diffusion coefficients D_1 and D_2 measured at the end of finite period. A mechanism for electrodiffusion of ions has been suggested[1]. The ions diffusing in the direction of field has a relatively longer relaxation time (τ_1) in jumping out of the old atmosphere and in the reverse direction has relatively shorter relaxation time (τ_2) as its old oppositively charged atmosphere tends to move with it under the action of the field. This concept also implies a difference in ion-atomsphere sizes, which results in difference in D_1 and D_2 values.

Experimental

Radioactive $H_2{}^{32}PO_4^-$ ions were obtained from Bhabha Atomic Research Centre, Bombay, and used as such after appropriate dilution. Electrolyte solutions (0.001 M) of sodium nitrate, potassium nitrate, sodium sulphate and potassium sulphate were prepared. The method for setting of the gel and measurements were reported earlier[1].

Acknowledgement

References

1. S. BALUJA and B. M. SHUKLA, J. Indian Chem Soc., 1996, 73, 233.

2. S. BALUJA and B. M. SHUKLA, Radiochim Acta, 1984, 37, 107.