



Diffusion of Fe^{3+} Ions in Agar Gel Medium Containing Transition Metal Sulfates at Different Electrolyte Concentration

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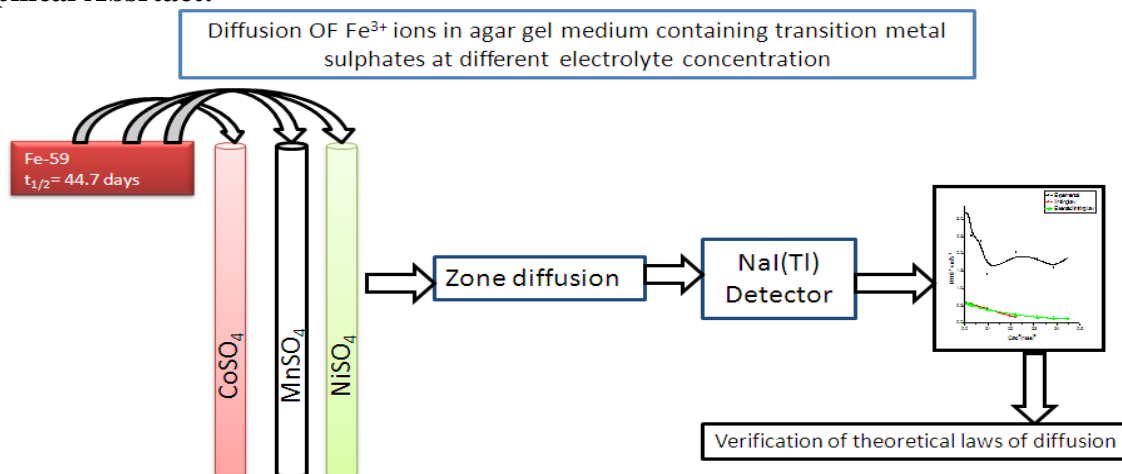
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ABSTRACT

The determination of diffusion coefficients of Fe^{3+} ions in agar gel medium containing MnSO_4 , CoSO_4 , NiSO_4 , CuSO_4 and ZnSO_4 electrolytes is discussed. The diffusion coefficients in various electrolytes are measured over a concentration range of 1×10^{-4} to 2×10^{-1} M using zone diffusion technique at 25°C . The obtained values are compared with the theoretically predicted values based on Onsager's theory and the observed deviations are accounted qualitatively on the basis of various interactions occurring in the ion-gel-water system.

Graphical Abstract:



Keywords: Diffusion, ferric ions, supporting electrolyte, transition metal sulfates.

INTRODUCTION

Tracer-diffusion of various univalent [1-3], bivalent [4-6] and trivalent [7] ions in different supporting electrolytes using different experimental conditions has been reported from this laboratory. Iron is an essential element [8, 9] playing a vital role in many cellular processes; Ferritin (Fe-III) is a measure for excess iron while, Ferric sulphate is used in dyeing industries, in pigments, as a coagulant or flocculants in wastewater treatment. In the present study the effect of electrolyte concentration on diffusion coefficients for diffusion of Fe^{3+} ions in agar gel medium containing various transition metal sulfates is studied. The diffusion coefficients were measured in 1.0 % agar gel using the zone diffusion technique [10, 11] at 25°C. The experimental diffusion coefficients thus obtained are compared with the theoretically predicted ones.

MATERIALS AND METHODS

Tracer diffusion of Fe^{3+} ions in different supporting electrolytes viz. MnSO_4 , CoSO_4 , NiSO_4 , CuSO_4 and ZnSO_4 was studied over a concentration range of 1×10^{-4} to 2×10^{-1} M in 1.0 % agar gel at 25°C. The diffusion coefficients were determined using labeled ^{59}Fe ions and the zone diffusion technique, the details of which are discussed in earlier paper [10]. ^{59}Fe ($t_{1/2}=44.7$ days) was obtained from BARC, Mumbai. The diffusion was allowed to proceed for 24 h and then the diffusion column was assayed by measuring the activity of Fe-59 at 1099 keV using NaI (TI) detector coupled with single channel analyzer. The diffusion coefficients were then calculated from the plots of log activity versus (distance)² and the values presented are an average of four independent measurements with a precision of $\pm 0.5\%$.

RESULTS AND DISCUSSION

The theoretical values of diffusion coefficient for diffusion of Fe^{3+} ions are calculated using the Onsager-Gosting-Harned equation [12, 13] given below:

$$D^* = \frac{RT\lambda^0}{|Z| F^2} - \frac{\lambda_j^0 |Z_j| F}{3N \epsilon} \times 2.694 \times 10^{16} \sqrt{\frac{4\pi}{\epsilon RT}} \times \left[1 - \sqrt{d(\omega_j)} \right] \times \sqrt{\sum C_i Z_i^2} \dots\dots\dots (1)$$

Where,

D^* is the diffusion coefficient of tracer ion,

R is gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$),

F is faraday constant (96500 C mol^{-1}),

ϵ is dielectric constant of water (78.5),

T is absolute temperature (298 K),

Z_i is the charge of diffusing ion,

λ^0 is the ionic conductance

C_i is concentration of the diffusing ion and

N is Avogadro's number.

The mobility function $d(\omega_j)$ in the above equation is a function of concentration, valence and limiting ionic conductance of ions in the solution. In deriving equation (1) the ions were treated as point charges, justifiable at very low concentrations only. However, at higher concentrations, one has to take into consideration the sizes of the ions present in the solution as they are reasonably close to each other. Taking this into account, Stokes et al.^[14] made empirical correction to the equation given by Onsager – Gosting – Harned by replacing \sqrt{C} by $\sqrt{C} / [(1+A'\sqrt{C})(1+A'\sqrt{C})/\sqrt{2}]$ where, $A'\sqrt{C} = \kappa a$, in which 'a' is the closest distance of approach of oppositely charged ions and κ is the reciprocal radius of the ionic atmosphere.

Table 1: Values of different parameters for the calculation of theoretical diffusion coefficient for tracer diffusion of Fe³⁺ ions in different systems.

Parameters	Electrolytes				
	ZnSO ₄	NiSO ₄	CoSO ₄	MnSO ₄	CuSO ₄
Z ₁	3	3	3	3	3
Z ₂	2	2	2	2	2
Z ₃	2	2	2	2	2
λ ⁰ ₁ /10 ⁻⁴ S m ² mol ⁻¹	68	68	68	68	68
λ ⁰ ₂ /10 ⁻⁴ S m ² mol ⁻¹	52.8	54.0	55.0	53.5	53.6
λ ⁰ ₃ /10 ⁻⁴ S m ² mol ⁻¹	80.0	80.0	80.0	80.0	80.0
d (ϖ _J)	0.591	0.594	0.596	0.593	0.593
A'	1.407	1.355	3.293	1.355	1.407

The values of different parameters involved in Eq. (1) for the calculation of theoretical diffusion coefficient for the different ions are recorded in table 1 shown above. By substituting these values into equation (1) the limiting law expressions for diffusion coefficient of Fe³⁺ ions in various electrolytes at 25°C take the following forms:

Fe³⁺ in NiSO₄

$$D_{\text{Fe}^{3+}}^* / 10^{-5} \text{ cm}^2 \text{ s}^{-1} = 6.03 - 9.826\sqrt{C} \quad \dots (2)$$

Fe³⁺ in CuSO₄

$$D_{\text{Fe}^{3+}}^* / 10^{-5} \text{ cm}^2 \text{ s}^{-1} = 6.03 - 19.64\sqrt{C} \quad \dots (3)$$

Fe³⁺ in ZnSO₄

$$D_{\text{Fe}^{3+}}^* / 10^{-5} \text{ cm}^2 \text{ s}^{-1} = 6.03 - 22.59\sqrt{C} \quad \dots (4)$$

Fe³⁺ in CoSO₄

$$D_{\text{Fe}^{3+}}^* / 10^{-5} \text{ cm}^2 \text{ s}^{-1} = 6.03 - 19.51\sqrt{C} \quad \dots (5)$$

Fe³⁺ in MnSO₄

$$D_{\text{Fe}^{3+}}^* / 10^{-5} \text{ cm}^2 \text{ s}^{-1} = 6.03 - 19.76\sqrt{C} \quad \dots (6)$$

Similarly, the extended limiting law expressions for D_{Fe³⁺}^{*} at 25°C take the following forms:

Fe³⁺ in NiSO₄

$$D_{\text{Fe}^{3+}}^* / 10^{-5} \text{ cm}^2 \text{ s}^{-1} = 6.03 - 9.826 \frac{\sqrt{C}}{(1 + 1.355\sqrt{C})(1 + 1.355\sqrt{C}/\sqrt{2})} \quad \dots (7)$$

Fe³⁺ in CuSO₄

$$D_{\text{Fe}^{3+}}^* / 10^{-5} \text{ cm}^2 \text{ s}^{-1} = 6.03 - 19.64 \frac{\sqrt{C}}{(1 + 1.407\sqrt{C})(1 + 1.407\sqrt{C}/\sqrt{2})} \quad \dots (8)$$

Fe³⁺ in ZnSO₄

$$D_{\text{Fe}^{3+}}^* / 10^{-5} \text{ cm}^2 \text{ s}^{-1} = 6.03 - 22.59 \frac{\sqrt{C}}{(1 + 1.407\sqrt{C})(1 + 1.407\sqrt{C}/\sqrt{2})} \quad \dots (9)$$

Fe³⁺ in CoSO₄

$$D_{\text{Fe}^{3+}}^* / 10^{-5} \text{ cm}^2 \text{ s}^{-1} = 6.03 - 19.51 \frac{\sqrt{C}}{(1 + 3.293\sqrt{C})(1 + 3.293\sqrt{C}/\sqrt{2})} \quad \dots (10)$$

Fe³⁺ in MnSO₄

$$D_{\text{Fe}^{3+}}^* / 10^{-5} \text{ cm}^2 \text{ s}^{-1} = 6.03 - 19.76 \frac{\sqrt{C}}{(1 + 1.355\sqrt{C})(1 + 1.355\sqrt{C}/\sqrt{2})} \quad \dots (11)$$

The theoretical values of diffusion coefficients of Fe^{3+} ions in different supporting electrolytes at various concentrations calculated using equations 2 to 11 are presented in tables 2 to 6 and are shown graphically in figures 1 to 5 as a function of square root of electrolyte concentration.

Table 2: Variation of tracer diffusion coefficient of Fe^{3+} ions with the concentration of NiSO_4 in 1 % agar gel at 25°C .

Conc./ M	$D_{\text{Fe}^{3+}}/10^{-5}\text{ cm}^2\text{ s}^{-1}$		
	Theoretical		Experimental
	Limiting law	Extended Limiting law	
0	0.603	0.603	-
5×10^{-4}	0.5833	0.5759	2.45
1×10^{-3}	0.5589	0.5444	2.38
5×10^{-3}	0.5406	0.5222	2.35
1×10^{-2}	0.4636	0.4394	2.27
5×10^{-2}	0.4059	0.3875	1.44
1.0×10^{-1}	0.1623	0.2372	2.11
1.5×10^{-1}	-	0.1727	2.14
2×10^{-1}	-	0.1404	1.97
2.5×10^{-1}	-	0.1215	1.98

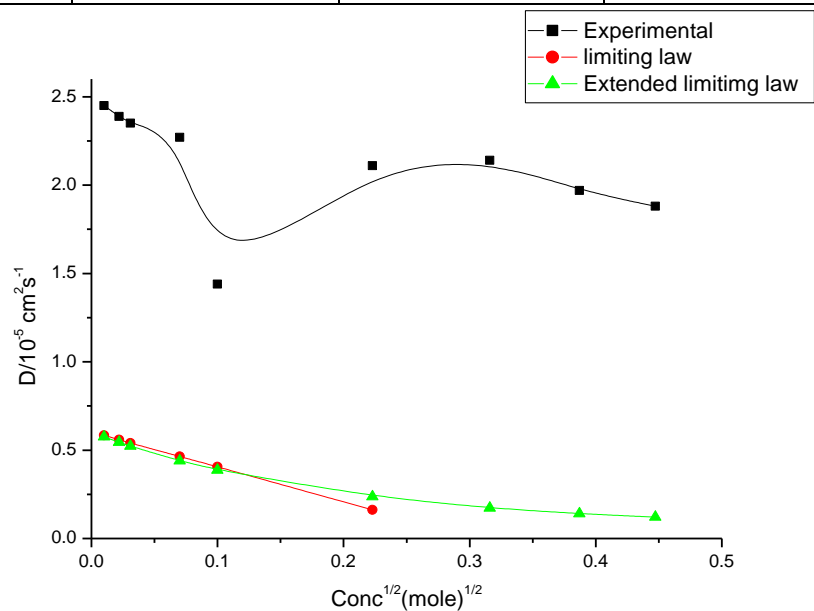


Fig 1: Variation of tracer diffusion coefficient of Fe^{3+} ions with square root of concentration of NiSO_4 in 1% agar gel at 25°C .

Table 3: Variation of tracer-diffusion coefficient of Fe⁺³ ions with the concentration of CuSO₄ in 1 % agar gel at 25⁰ C.

Conc./ M	D Fe ³⁺ /10 ⁻⁵ cm ² s ⁻¹		
	Theoretical		Experimental
	Limiting law	Extended Limiting law	
0	0.603	0.603	-
5x10 ⁻⁴	0.5833	0.5759	2.15
1x10 ⁻³	0.5590	0.5446	2.04
5x10 ⁻³	0.5408	0.5224	1.77
1x10 ⁻²	0.4641	0.4405	1.67
5x10 ⁻²	0.409	0.3895	1.94
1.0x10 ⁻¹	0.1638	0.2436	2.10
1.5x10 ⁻¹	-	0.1823	2.31
2x10 ⁻¹	-	0.1523	2.34
2.5x10 ⁻¹	-	0.1350	2.50

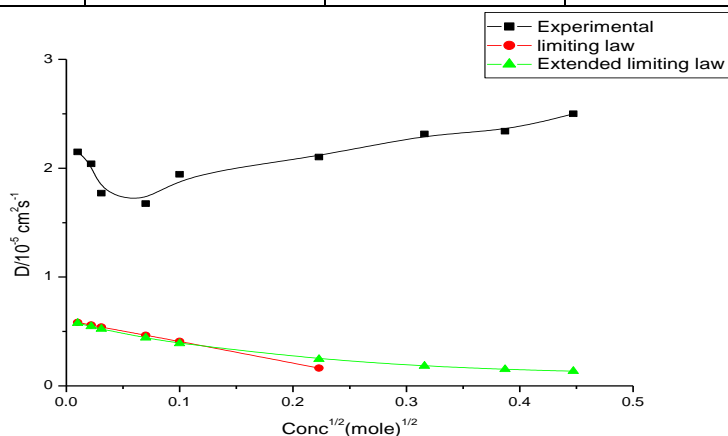


Fig 2: Variation of tracer diffusion coefficient of Fe³⁺ ions with square root of concentration of CuSO₄ in 1% agar gel at 25⁰C.

Table 4: Variation of tracer-diffusion coefficient of Fe⁺³ ions with the concentration of ZnSO₄ in 1 % agar gel at 25⁰ C.

Conc./ M	D Fe ³⁺ /10 ⁻⁵ cm ² s ⁻¹		
	Theoretical		Experimental
	Limiting law	Extended Limiting law	
0	0.603	0.603	-
5x10 ⁻⁴	0.5831	0.5757	3.31

1×10^{-3}	0.5587	0.5441	2.46
5×10^{-3}	0.5403	0.5217	2.03
1×10^{-2}	0.4629	0.4391	1.79
5×10^{-2}	0.4049	0.3876	1.44
1.0×10^{-1}	0.1600	0.2405	2.15
1.5×10^{-1}	-	0.1786	2.24
2×10^{-1}	-	0.1484	2.25
2.5×10^{-1}	-	0.1310	2.37

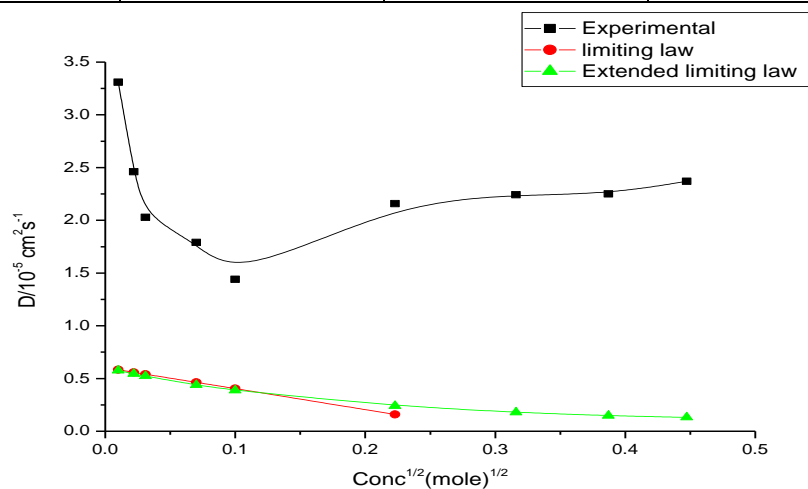


Fig 3: Variation of tracer diffusion coefficient of Fe^{3+} ions with square root of concentration of $ZnSO_4$ in 1% agar gel at $25^\circ C$.

Table 5: Variation of tracer-diffusion coefficient of Fe^{3+} ions with the concentration of $CoSO_4$ in 1% agar gel at $25^\circ C$.

Conc./ M	$D Fe^{3+} / 10^{-5} cm^2 s^{-1}$		
	Theoretical		Experimental
	Limiting law	Extended Limiting law	
0	0.603	0.603	-
5×10^{-4}	0.5834	0.5771	2.07
1×10^{-3}	0.5593	0.5494	1.87
5×10^{-3}	0.5413	0.5314	1.63
1×10^{-2}	0.4650	0.4746	1.55
5×10^{-2}	0.4079	0.4468	1.64
1.0×10^{-1}	0.1667	0.3984	1.72

1.5×10^{-1}	-	0.3936	1.78
2×10^{-1}	-	0.3966	1.80
2.5×10^{-1}	-	0.4012	1.75

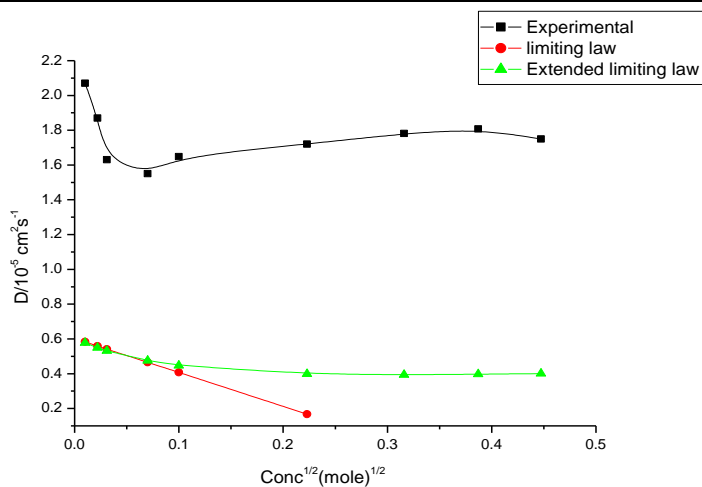


Fig 4: Variation of tracer diffusion coefficient of Fe³⁺ ions with square root of concentration of CoSO₄ in 1% agar gel at 25°C.

Table 6: Variation of tracer-diffusion coefficient of Fe⁺³ ions with the concentration of MnSO₄ in 1 % agar gel at 25⁰ C.

Conc./ M	DFe ³⁺ /10 ⁻⁵ cm ² s ⁻¹		
	Theoretical		Experimental
	Limiting law	Extended Limiting law	
0	0.603	0.603	-
5×10^{-4}	0.5832	0.5757	3.17
1×10^{-3}	0.5588	0.5441	3.03
5×10^{-3}	0.5405	0.5217	2.52
1×10^{-2}	0.4632	0.4384	2.37
5×10^{-2}	0.4054	0.3862	1.41
1.0×10^{-1}	0.1611	0.2350	2.03
1.5×10^{-1}	-	0.1700	1.85
2×10^{-1}	-	0.1376	1.61
2.5×10^{-1}	-	0.1186	1.70

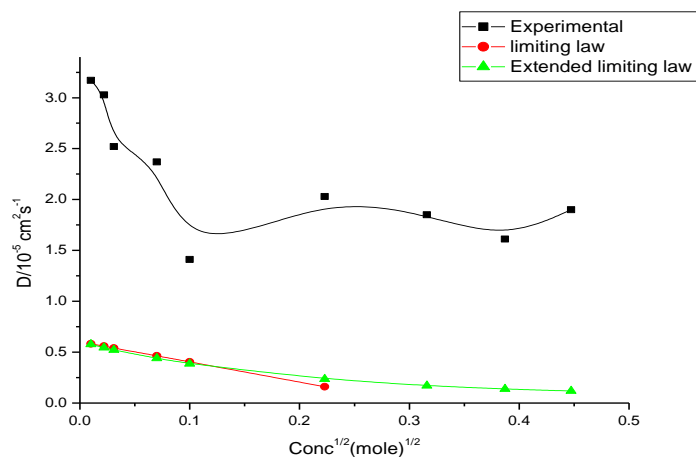


Fig 5: Variation of tracer diffusion coefficient of Fe^{3+} ions with square root of concentration of MnSO_4 in 1% agar gel at 25°C .

As, observed from tables 2-6 and figs.1-5, the theoretical value of $D_{\text{Fe}^{3+}}^*$ is always less than the experimental value at all the concentrations in the systems studied. Further, a minimum in $D_{\text{Fe}^{3+}}^*$ versus \sqrt{C} plot is a characteristic feature of all the systems (Figures 1 to 5) and is present at 5×10^{-2} M in NiSO_4 , ZnSO_4 and MnSO_4 at 1×10^{-2} M in CuSO_4 and CoSO_4 systems while, there is an absence of such a minima in the theoretical curves.

The deviations observed between the theoretical and experimental values of diffusion coefficients can be explained qualitatively on the basis of various interactions occurring in ion-gel-water system as discussed in earlier reports from this laboratory [7, 15, 16]. The observed higher experimental values of diffusion coefficients than the theoretically expected values for all the concentrations in the system studied are attributed to the dominance of the gel-water interactions. At higher concentrations, however, adsorption and obstruction effects are known to decrease with electrolyte concentration^{[17],[18]}. Thus, the contribution of the diffusion retarding effects of adsorption and obstruction is reduced at higher concentrations and hence the gel-water interaction becomes more prominent at these concentrations. The overall effects of all these interactions led to higher values of diffusion coefficients than that predicted by theory at higher concentrations in all the systems. The values in the tables 2 to 6 indicate the deviations of experimental diffusion coefficients from the theoretical values with concentration for a particular system are found to vary from system to system.

It is also evident from the figures that at all concentrations the experimental values are not only higher than the theoretical, but even shows a change in the trend of the D_{expt} versus \sqrt{C} plots. The measured values of diffusion coefficients increase with concentration and this reversal in the trend of diffusion coefficient with concentration gives rise to a minimum in the curve. The occurrences of such minima in D_{expt} versus \sqrt{C} curves have been reported by several workers both in gel [19, 20] as well as pure aqueous media [21- 23]. The occurrence of a minimum in the D_{expt} versus \sqrt{C} plot can be explained qualitatively on the basis of Wang's[21] model, which considers the changes in the physical properties taking place at the microscopic level with increasing electrolyte concentration. Wang suggested that at the lower concentration, the ions are fully hydrated hence; any distortion present in the solvent water immediately surrounding each hydrated ion is the same as that existing at infinite dilution, since average distance between the ions is very large, hydration and ion-solvent interaction remain the same. The only effect of increasing electrolyte concentration in this range is to increase the long-range ionic attraction (i.e. the relaxation effect) which gives a decreasing trend in the D_{expt} with increasing concentration of electrolyte in the systems studied.

When the concentration of electrolyte increases, the distance as well as the number of water molecules between the two ions goes on reducing and it becomes increasingly difficult for water molecules to orient themselves and maintain the stable semi-crystalline structure of water, which exists at infinite dilution. Hence, the semi-crystalline structure of water gets distorted which leads to a decrease in the local dielectric constant of the solvent water. This decrease in dielectric constant increases the self-energy of the ions in the normal state, while the energy of the activated state remains unaffected. Thus, the total energy barrier for diffusion of ions is reduced leading to an increase in diffusion coefficient with increasing concentration of the electrolyte as observed.

APPLICATIONS

The study can be used to verify the theoretical concepts and laws of diffusion process.

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REFERENCES

- [1] S. F. Patil, N. G. Adhyapak, S. S. Joshi, "Effect of supporting electrolyte on the activation energy for diffusion of some mono-valent ions", *Int. J. Appl. Radiat. Isot.*, **1985**, 95, 201–209.
- [2] N.S. Rajurkar, N.A. Gokarn, "Diffusion of cesium ions labeled with Cs-134 agar gel containing alkali metal chlorides: Obstruction Effect and Activation Energy", *J. Mol. Liq.*, **2005**, 122, 49–54.
- [3] N.A. Gokarn, N.S. Rajurkar, "Diffusion of cesium ions labeled with 134Cs in agar gel containing alkali metal iodides: Obstruction effect and activation energy", *J. Solution Chem.*, **2006**, 35, 507–517.
- [4] S.F. Patil, N.G. Adhyapak, "Self diffusion of Zn(II) in agar gel", *Int.J. Appl. Radiat. Isot.*, **1981**, 32, 887–889.
- [5] S. F. Patil, N.G. Adhyapak, S.K. Ujalambkar, "Trace-ion diffusion of $^{54}\text{Mn}^{2+}$ in 2-1 electrolytes in agar gel", *Radiochem. Radioanal. Lett.*, **1981**, 49, 119–128.
- [6] S.F. Patil, N.G. Adhyapak, "Obstruction effect of a gel in diffusion of cadmium acetate and cadmium ions", *Radiochem. Radioanal. Lett.*, **1982**, 52, 177–184.
- [7] N.S. Rajurkar, M.M. Kute, "Tracer Diffusion of Cr^{3+} Ions in Agar Gel Media Containing Transition-Metal Sulfates", *J.Chem. Eng. Data*, **2010**, 55, 1804-1807.
- [8] Rashmi. Kumar, Nilima. Rajurkar, Parag. Adhyapak, "Elemental profile and Hb content in whole blood of adolescence from Baramati region-Pune, Maharashtra", *J Applicable Chem.*, **2016**, 5(4), 886-893.
- [9] Vijay j. Ghodvinde, S. M. Pitale et.al, "New analytical technique for determination of trace amount of Fe(III) by using UV-Visible spectrophotometric method with photometric reagent", *J Applicable Chem.*, **2017**, 6(1), 107-114.
- [10] N.S. Rajurkar, S. Jha, N.A. Gokarn, "Applications of NAA in diffusion studies", *J. Radioanal. Nucl.Chem.*, **2001**, 250, 143.
- [11] N.S. Rajurkar, N.A. Gokarn, "Diffusion of cesium ions labeled with 134Cs in agar gel containing alkali metal chlorides: obstruction effect and activation energy", *J. Mol. Liq.*, **2005**, 122, 49.
- [12] L. Onsager, "Theories and problems of liquid diffusion", *Ann. N.Y. Acad.Sci.*, **1945**, 46, 241–245.
- [13] L. J. Gosting, H. S. Harned, "The measurement of self-diffusion with new continuous monitoring method", *J. Am. Chem. Soc.*, **1951**, 73, 159–163.
- [14] R. H. Stokes, E. A. Wolff, R. Mills, "Tracer diffusion of iodide ion in aqueous chloride solutions at 25 °C", *J. Phys. Chem.*, **1957**, 61, 1634–1636.
- [15] N. S. Rajurkar, N. A. Gokarn, "Studies on self and electrolyte diffusion in cesium halides", *Appl. Radiat. Isot.*, **2003**, 58, 441–444.
- [16] S. F. Patil, N.G. Adhyapak and S. K. Ujalambkar, *Radiochem. Radional. Lett.*, **1981**, 49, 119.

- [17] A. G. Langdon, H. C. Thomas, "Self-diffusion studies of gel hydration and the obstruction effect" *J. Phys. Chem*, **1971**, 75, 1821–1824.
- [18] N.S. Rajurkar, M.M. Kute, "Study of obstruction effect and activation energy for tracer diffusion of chromium ions in agar gel containing transition metal sulphates", *J. Mol. Liq*, **2008**, 142, 6–9.
- [19] N.A. Gokarn, N.S. Rajurkar, "Diffusion of cesium ions in agar gel containing alkali metal bromides", *J. Solution Chem*, **2006**, 35, 1673–1685.
- [20] S.F. Patil, N.G. Adyapak, "Self-diffusion of chromate ion in agar gel", *Int. J. Appl. Radiat. Isot*, **1981**, 32, 631–635.
- [21] J.H. Wang, "Tracer diffusion in liquids. I. Diffusion of tracer amount of sodium ions in aqueous potassium chloride solutions", *J. Am. Chem.Soc*, **1952**, 74, 1182–1185.
- [22] H.G. Hertz, M. Holtz, R. Mills, "Effect of structure on ion self diffusion in concentrated electrolyte solutions", *J. Chim. Phys. Physiochim. Biol*, **1974**, 71, 1355–1362.
- [23] R. Mill, "Tracer-ion diffusion in electrolyte solutions", *ReV. Pure Appl. Chem*, **1961**, 11, 78–91.

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