Diffusion of Fe^{3+} Ions in Agar Gel Medium Containing Zinc Sulfate: Obstruction effect and Activation Energy

M. S. Gupte

Department of Chemistry, Modern College of Arts, Science and Commerce, Ganeshkhind
Pune-411053, India

Email:mohinigupte@moderncollegegk.org

Abstract

The paper presents a study on the diffusion behaviour of ferric ions within an agar gel medium containing zinc sulfate electrolyte. Investigations for various aspects, including the obstruction effect introduced by the agar gel, the validation of Wang's diffusion model, and the suitability of applying transition state theory to the diffusion of Fe^{3+} ions in an agar gel medium with zinc sulfate were made. This investigation involved optimising the gel concentration, electrolyte concentration, and system temperature. The diffusion coefficients are determined by the zone diffusion technique. The results reveal that the activation energy (E) decreases as the electrolyte concentration increases, aligning with Wang's model. This decrease is attributed to the disruption of the water structure induced by ions and agar molecules. Additionally, for a fixed electrolyte concentration, the activation energy decreases with the cubic root of the weight percent of agar ($W^{1/3}$), while the diffusion coefficient (Do) decreases with the square of the reciprocal of the weight percent of agar ($W^{-2/3}$). This behaviour is consistent with the principles of the transition state theory of diffusion.

Keywords: Diffusion, Ferric ions, Supporting electrolyte, Obstruction effect, Tracer diffusion, Transition state theory.

1.Introduction:

Diffusion is one of the most fundamental irreversible processes by which equalization of concentration is achieved by spontaneous flow of matter from higher concentration to lower concentration region regardless of gravitational forces. When an ion at very low concentration diffuses into a solution of an electrolyte with uniform composition is termed as tracer diffusion. A lot of work on diffusion of ions in various fields is being carried out in different media [1-5]. The experimental methods for determination of diffusion coefficient, 'D' encounter certain difficulties in obtaining accurate data on diffusion due to turbulent flow, the very accurate control of temperature and analytical accuracy. These errors in the study of diffusion are reduced to a minimum by immobilizing the system in gel medium, which has been reported by many researchers [6,7]. Various aspects of tracer diffusion, such as the effect of electrolyte concentration[8], gel concentration [9, 10] and temperature [9, 10] in different systems have been studied and reported in a series of research papers from our laboratory. The present work deals with the effect of temperature and concentration of electrolyte on the obstruction effect for tracer diffusion of Fe^{3+} ions in zinc sulphate to confirm the Wang's model[11].

The study involved an investigation of these variables through the measurement of diffusion rates within a medium with gel concentrations ranging from 1.0% to 2.5%. To assess the impact of temperature on hindrance effects, diffusion coefficients for the movement of Fe^{3+} ions were determined at different temperatures, each at a concentration of 0.1 M. Additionally, studies were performed to understand the suitability of transition state theory by altering gel concentrations within a temperature range of 25°C to 45°C and maintaining a fixed concentration of $ZnSO_4$ at 0.1M.

2. Experimental:

The diffusion process was allowed to progress for a duration of 24 h, and we monitored the diffusion column by measuring the activity of Fe-59 at different column lengths. These measurements were carried out using a NaI (Tl) detector in conjunction with a single-channel analyzer operating at 1099 keV.

In the initial series of experiments, we determined the obstruction effect and activation energy for Fe^{3+} ions in a solution of 0.1M zinc sulfate. This investigation involved different gel concentrations ranging from 1.0% to 2.5% and was carried out across a temperature range

of 25°C to 45°C. In the subsequent set of experiments, we focused on determining the activation energy for the tracer diffusion of Fe^{3+} ions in a 1% agar gel containing zinc sulfate electrolyte at concentrations ranging from 0.001 to 0.2M. This analysis was conducted over the temperature range of 25°C to 45°C. The activation energies were calculated by applying the Arrhenius equation through a least square fitting of the diffusion data, as provided below:

$$D = D_o e^{-E/RT}$$ ……………………(1)

where E is activation energy for diffusion process and Do is the diffusion coefficient at very high temperature respectively.

3. Results and discussion:

3.1. Effect of gel concentration: Effect of gel on diffusion process is shown in Fig.1. As can be seen from this figure, the diffusion coefficient decreases linearly with the weight fraction of agar, which obeys the following equation [12,13].

$$D_g = D_s - a\omega$$ …………….(2)

Where Dg and Ds are diffusion coefficient in gel medium and extrapolated value of D_g to zero agar content while 'a' represents the slope of the plot of Dg versus ω.

The reduction in the diffusion coefficient as the concentration of gel increases (Table 1) is ascribed to the three-dimensional network formed by the larger agar macromolecules, which possess a considerably smaller diffusion coefficient due to their higher molecular weight compared to the diffusing ions. These substantial and relatively immobile macromolecules impede the movement of ions. When an ion is in close proximity to an agar molecule, it must travel along a longer path to reach the other side of the molecule. This extended diffusion path becomes more pronounced with the gel concentration increases, leading to a corresponding decrease in the diffusion coefficient.

As depicted in Fig. 1, the slope of the Dg versus ω plot decreases with an increasing concentration of electrolyte. The hindrance effect can be quantified using the parameter α, which signifies the relative reduction in the diffusion coefficient concerning the weight fraction of agar. This is calculated by dividing the slope of the plot 'a' by Ds. The hydration

value of agar (H), expressed as the amount of bound water in grams per gram of anhydrous agar, is determined for various systems using the following equation [14]

$$\alpha = \left[\frac{1}{da} + \frac{H}{dw}\right] . d_w (\beta - 1) \qquad\qquad\qquad ……………..(3)$$

where, da (1.6) is density of agar, dw is the density of pure water and β (5/3) is the shape factor for agar molecules.

The values of α and H are reported in Table 2.

An examination of Table 2 reveals a consistent trend: as the concentration of the electrolyte increases, both the values of α and H decrease. This trend can be understood by considering the concept of competitive hydration between ions and agar macromolecules within a given system, and it aligns with findings from our previous reports (references [9, 10, 12].

The degree of hydration of agar (referred to as H) is influenced by the presence of different ions due to the stronger attractive forces these ions exert on water molecules. In a system containing both ions and agar molecules, there exists a competition for water molecules to facilitate hydration. The extent of agar hydration is contingent on the concentration of ions in the system.

As the concentration of the electrolyte increases, there is a greater number of ions competing with agar molecules for hydration. Consequently, less water is available for the hydration of agar, leading to a reduction in the extent of agar hydration. This, in turn, results in a decrease in the value of 'H' and a decrease in the slope of Dg versus ω, indicating a reduction in Dg concerning the weight percentage of agar, as well as a decrease in $\alpha = a/Ds$ as the concentration of the electrolyte increases, as observed.

The effect of gel concentration on the activation energy required for diffusion in different systems at a specified concentration of diffusing species is investigated over the temperature range of 25-45^{0}C. A plot of log D as function of 1/T is shown in Fig.2 at different gel percentages (1-2.5%) for diffusion of Fe^{3+} ions at 0.1M concentration of $ZnSO_4$.

As the temperature of the system rises, it becomes evident that the diffusion coefficient also increases within each system. This phenomenon can be explained by referencing the principles of the transition state theory of diffusion [15,16]. Since we are measuring these diffusion coefficients in an agar gel medium, it is essential to consider the influence of the

temperature on the agar gel. Nevertheless, it has been demonstrated that the obstructive impact created by the agar gel remains constant regardless of temperature variations. This finding implies that the gel's structure remains unaltered within the temperature range investigated (25°C–45°C). Consequently, alterations in temperature solely affect the diffusion process. When the temperature is elevated, a significant proportion of the diffusing particles attains the necessary energy level to surmount the potential energy barrier associated with diffusion. This results in an upward trend in the diffusion coefficient with temperature, in alignment with the principles of the transition state theory of diffusion.

Table 2 presents the activation energy (E) and Do values, which were determined through least squares fitting of the data using the Arrhenius equation. The standard deviation is also included. Upon examining Table 2, it becomes evident that both E and Do values exhibit a decline as the gel concentration within the studied system increases. This observation aligns with expectations derived from prior research on different systems and can be adequately elucidated through the framework of the transition state theory of diffusion.

The reduction in the Do value with increasing gel concentration suggests that the jump distance (λ) value should also decrease as gel concentration rises. Imagining a scenario of cubic packing within the liquid, one can envision a molecule oscillating around the origin with its six closest neighbours firmly positioned along the three axes. In this geometric context, each molecule is anticipated to be situated at a distance of $V^{1/3}$ from the origin, where V denotes the volume. Consequently, when considering diffusion in a single direction, the λ value is expected to vary with $V^{1/3}$, and therefore with $W^{1/3}$, where W signifies the weight percentage of agar.

Given that Do is directly proportional to λ^2, it is anticipated to vary with $W^{-2/3}$. This relationship is corroborated by an observed linear association in the Do versus $W^{-2/3}$ plot, as illustrated in Fig.3. Moreover, the apparent pattern in the behaviour of Do and, consequently, gel percentage suggests that the presence of agar macromolecules inhibits longer elementary movements, allowing only shorter jumps as the gel concentration increases. This diminishing trend in activation energy with higher gel concentration aligns with this hypothesis, as depicted in Figure 4. It's worth noting that the activation energy demonstrates a linear relationship with the one-third power of gel percentage ($W^{1/3}$) in the investigated systems.

Conclusions:

Studies on effect of gel concentration on diffusion of Fe^{3+} ions in $ZnSO_4$ electrolyte reveals that as the concentration of the electrolyte increases, obstruction effect due to agar macromolecules measured in terms of α and extent of hydration of agar expressed in terms of H decrease. Further, Arrhenius parameters, E and Do decrease with increasing gel concentration ; E is found to vary with $W^{1/3}$ and Do with $W^{-2/3}$.
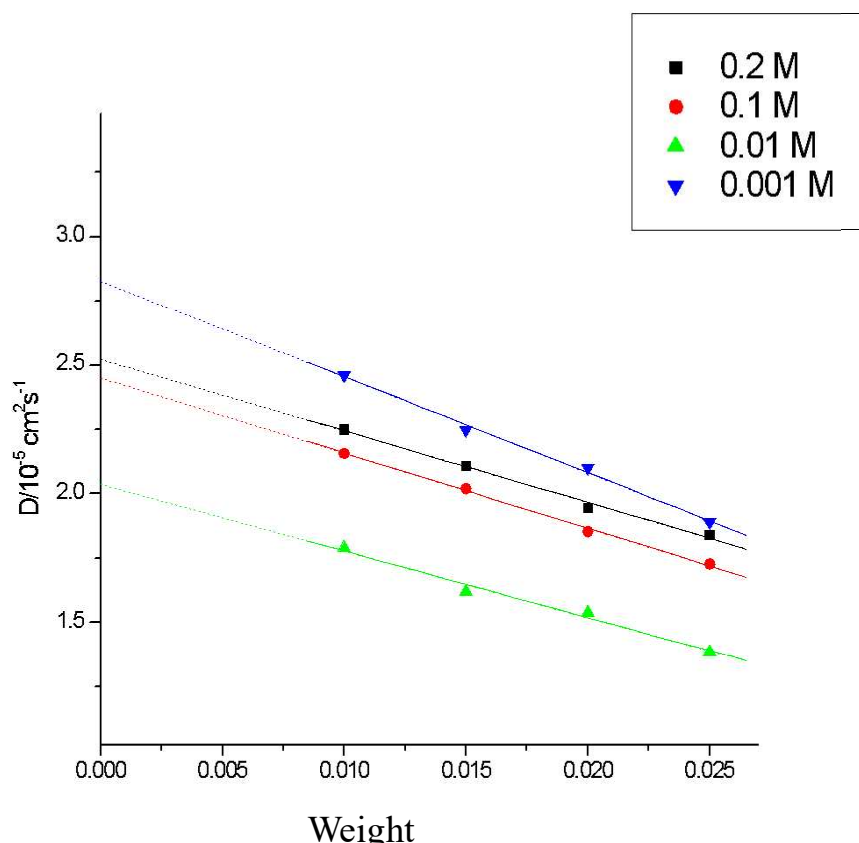
Figures

Fig.1: Obstruction effect in the tracer diffusion of Fe^{3+} ions at different concentrations of $ZnSO_4$ at 25^0C.
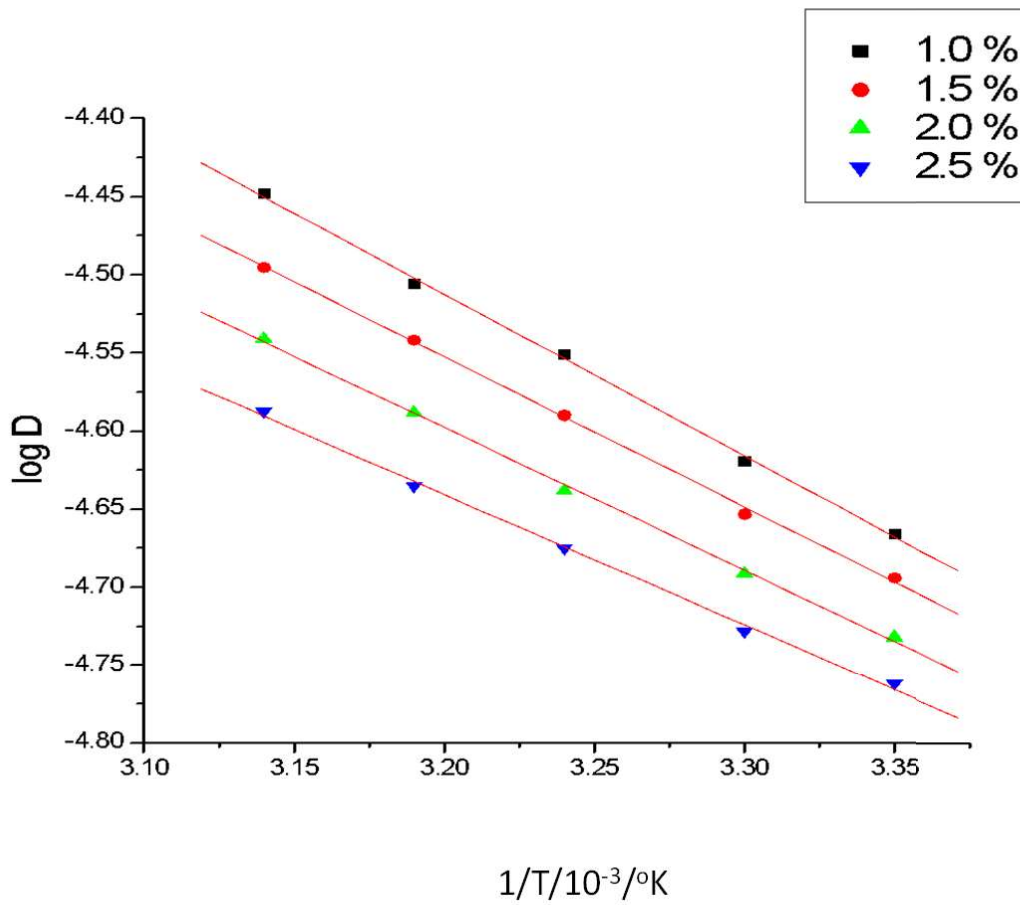
Fig.2: Activation energy for the tracer diffusion of Fe^{3+} in agar gel medium containing $ZnSO_4$ (0.1 M) with various gel concentrations.
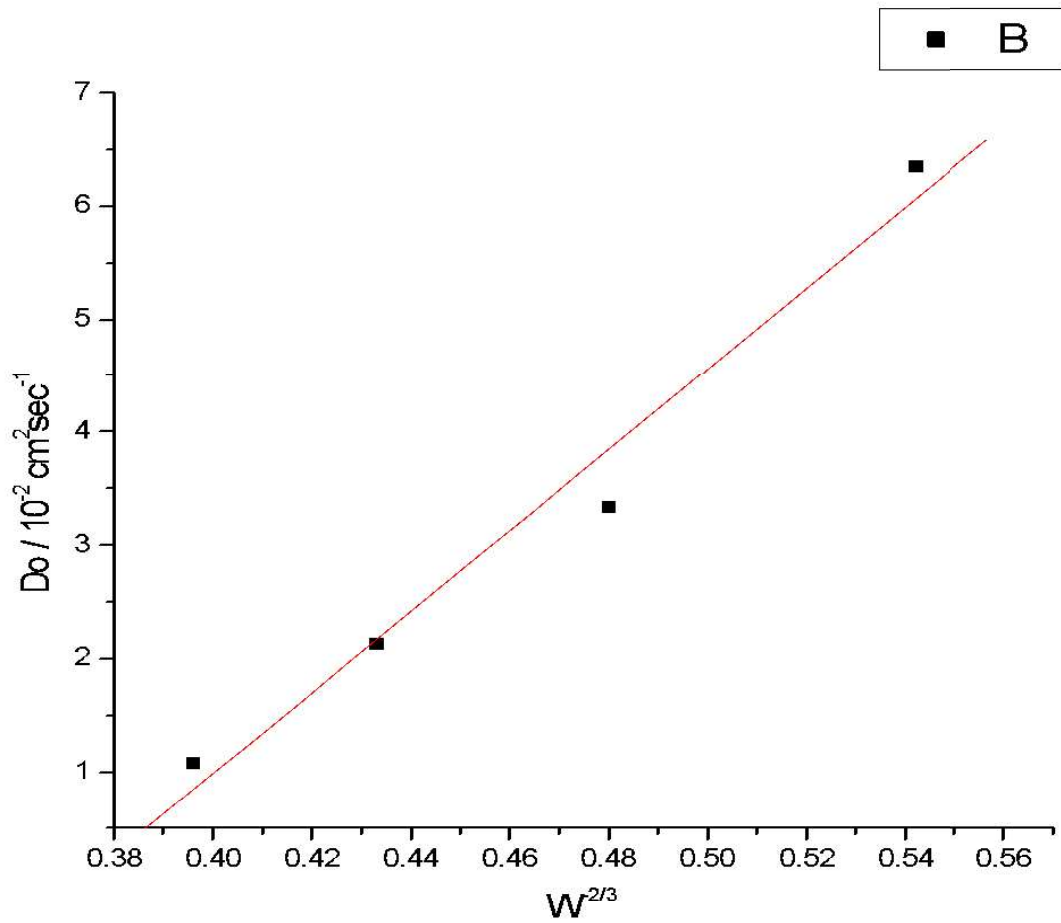
Fig.3: Variation of D_0 with $W^{-2/3}$ for tracer diffusion of Fe^{3+} ions in agar gel medium containing ZnSO$_4$ (0.1 M).
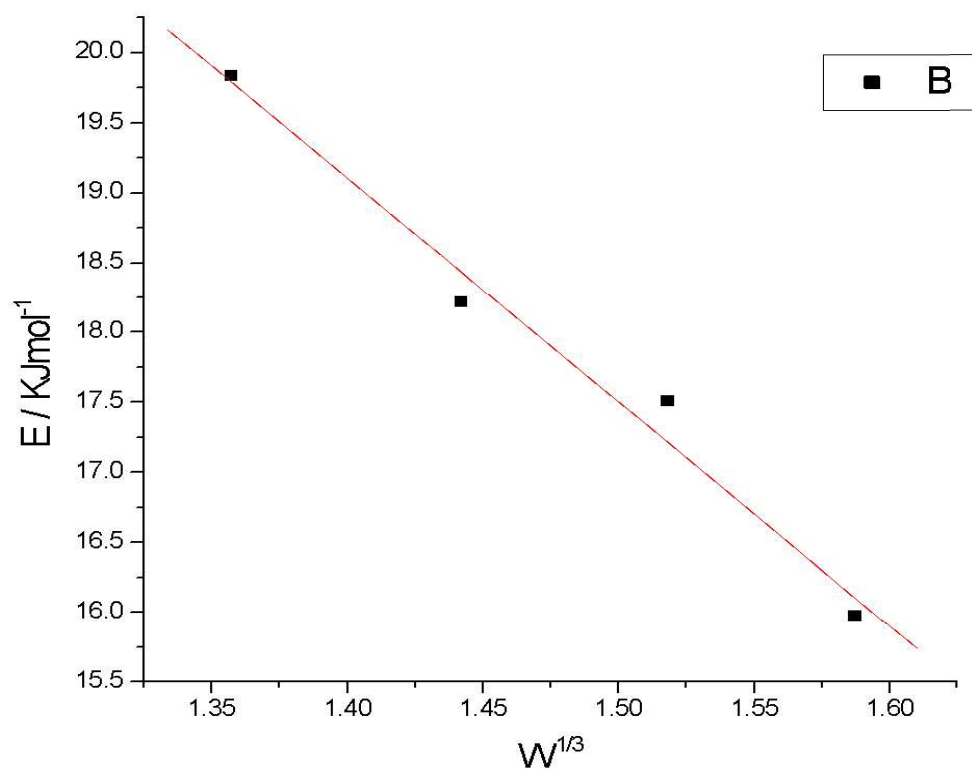
Fig.4: Variation of E with $W^{1/3}$ for tracer diffusion of Fe^{3+} ions in agar gel medium containing $ZnSO_4$ (0.1M).

Tables

Table 1: Variation of tracer diffusion coefficient of Fe^{+3} ions with weight fraction of agar at different $ZnSO_4$ concentrations at 25^0 C.

ω (weight fraction) of Agar $\downarrow$	D^* Fe^{3+} / 10^{-5} cm^2 s^{-1}			
$ZnSO_4$Concentration/M$\rightarrow$	**0.2**	**0.1**	**0.01**	**0.001**
0.010	2.25	2.158	1.79	2.46
0.015	2.108	2.02	1.621	2.25
0.020	1.945	1.853	1.54	2.1
0.025	1.842	1.728	1.386	1.89

Table 2: Variation of $\propto$ and Hydration value of agar in terms of grams of bound water per gram of anhydrous agar for tracer diffusion of Fe^{+3} ions in $ZnSO_4$.

$ZnSO_4$ Concentration / M	$\propto$	H
0.001	13.16	19.13
0.01	12.69	18.43
0.1	11.89	17.22
0.2	11.0	15.89

Table 3: Variation of E and Do with gel concentration for tracer diffusion of Fe^{+3} ions in $ZnSO_4$.

Gel percentage	E/kJmole^{-1}	Do/10^{-2} cm^{2}s^{-1}
1.0	19.84±0.4	6.36±0.021
1.5	18.40±0.3	3.34±0.010
2.0	17.51±0.3	2.13±0.006
2.5	15.98±0.4	1.08±0.004

References:

1. J. Wang, L. Zhang, J. Xue, G. Hu, Biomicrofluidics, 8, 024118, 2014.

2. A. Revil, D. Jougnot, Journal of Colloid and Interface Science, 319 (1), 226, 2008.

3. E. Quartarone, S. Davino, E. Lufrano, L. Coppola, C. Simari, and I. Nicotera*, ChemElectroChem,10(6),1, 2023.

4. C. Pean, B. Daffos, B. Rotenberg, P. Levitz, M. Haefele, P. Taberna, P. Simon, and M. Salanne, Journal of the American Chemical Society, 137 (39), 12627, 2015.

5. P. Banerjee, B. Bagchi, J. Chem. Phy., 150, 190901, 2019.

6. H. J. Arnikar and S. A. Tattithali, 21(4), 2680,1989.

7. Z. Fricke, Electrochem., 31, 430, 1925.

8. N.A. Gokarn, N.S. Rajurkar, J. Mol. Liq. 129, 129, 2006.

9. N.S. Rajurkar, M.M. Kute, J. Mol. Liq. 142, 6, 2008.

10. N.S. Rajurkar, N.A. Gokarn, J. Mol. Liq. 122, 49, 2005.

11. J. H. Wang, J. Am. Chem. Soc. 74, 1182, 1952.

12. A. V. Borhade, J. Radioanal. Nucl. Chem. 257, 323, 2003.

13. N.S. Rajurkar, M.M. Kute, J. Sol. Chem., 39, 87, 2010.

14. J.H. Wang, J. Am. Chem. Soc. 33, 4755, 1954.

15. S. Glasstone, K. J. Laidler, H. Eyring, McGraw-Hill, New York, 1941.

16. H. Eyring, J.F. Kincaid, A. E. Stearn, Chem. Rev. 28, 301, 1941.