



—● SUMMARY ●—

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The thesis presents the work done on tracer-diffusion of some labelled transition metal ions in different transition metal chlorides and sulphates as well as electrolyte-diffusion of manganese chloride, manganese sulphate and copper sulphate labelled with respective cations in agar gel medium. It consists of four chapters : The first chapter is an introductory one, the second chapter covers the experimental part and the third and fourth chapters deal with the discussion of the results obtained in the present studies.

The first chapter covers the introduction of the subject of diffusion and related theories. Onsager and Onsager-Fuoss theories of self- and electrolyte-diffusion respectively are discussed in detail from which the corresponding equations of diffusion coefficient are derived. It also includes a brief discussion of the transition state theory as applied to the phenomenon of diffusion. At the end of this chapter, the work done on self- and electrolyte-diffusion studies by earlier workers both in solution state and in gel medium is reviewed briefly.

The principle of zone-diffusion technique used for determining the diffusion coefficient is discussed in Chapter 2 along with the boundary conditions of the technique. A solution of the Fick's II law for the given boundary conditions is derived. The expression thus obtained was used for calculating the experimental diffusion coefficient.

The applicability of the Onsager and Onsager-Fuoss theory to the experimental data of tracer and electrolyte-diffusion coefficients respectively, obtained for various systems is examined in Chapter 3 and the corresponding results are discussed in two separate sections.

Section A deals with the studies on tracer-diffusion of Mn^{2+} , Cu^{2+} and Zn^{2+} ions in different supporting electrolytes while Section B presents the results of electrolyte-diffusion of $MnCl_2$, $MnSO_4$ and $CuSO_4$ over a wide range of concentration of $25^\circ C$.

The more important observations related to the tracer-diffusion studies (Section A) are summarized below.

(1) A minimum in the experimental D^* versus \sqrt{C} curve at lower concentrations is a characteristic of all the systems studied against its absence in the theoretical curve.

(2) D_{expt}^* is found to be lower than the D_{theo}^* at lower concentrations while the reverse is observed at higher concentrations with the exception of the results obtained in tracer-diffusion of Cu^{2+} ions.

(3) Initially the diffusion coefficient decreases with concentration of the electrolyte in qualitative agreement with the theory but beyond a certain concentration it starts increasing.

These discrepancies in the observed results over the entire range of concentration are explained on the basis of gel-water, ion-water and ion-ion interactions as well as adsorption and obstruction effects due to the gel macromolecules. The increasing trend of diffusion coefficient after the minimum is accounted with the help of Wang's model which considers the changes in the physical properties occurring at the microscopic level at higher concentrations of the electrolyte due to ion-ion and ion-water interactions. These results are also interpreted in terms of structure-breaking properties of the ions affecting the sizes of ion-water aggregates by decoupling of the hydrogen bonds (Hertz et al. model).

In Section B of this chapter, the results on electrolyte-diffusion studies are discussed, the important observations being :

(1) The experimental value of diffusion-coefficient is always less than the theoretical one in MnCl_2 and MnSO_4 systems and upto 10^{-3} M concentration in CuSO_4 system.

(2) The minimum in the experimental D' versus \sqrt{C} curve occurs at concentration which is very much lower than that predicted by the theory in all the systems studied.

The observed results are explained in terms of different types of interactions occurring in gel-water-electrolyte system. The shift in the experimental minimum towards the lower concentration side in relation to the theoretical minimum, is attributed to desolvation of the ions with increasing concentration of the electrolyte.

The effect of gel macromolecules on diffusion is studied elaborately in Chapter 4 by varying the gel concentration as well as temperature of the system. Section A of this chapter deals with the study of obstruction effect in different systems while Section B consists of determination of activation energy for the process of diffusion for different ions and electrolytes.

The study of obstruction effect under different conditions of temperature and concentration of the electrolyte leads to the following observations :

- (1) For a particular concentration of the electrolyte, obstruction effect calculated in terms of α is independent of temperature.
- (2) At a given temperature, α -value decreases with increasing concentration of the electrolyte,
- (3) For a particular system, the α -value is higher for electrolyte-diffusion as compared to that for self-diffusion.
- (4) In tracer-diffusion, the α -value decreases with increasing charge density of cation of the electrolyte.
- (5) In all the systems, experimental value of α is found to be very much greater than that predicted by the theory.

Higher value of α compared to the theoretical one is attributed to the extensive hydration of agar macromolecules. Further, the higher value of α observed for electrolyte-diffusion than that for self-diffusion process, for a given concentration of the electrolyte and decreasing trend in it with concentration of the electrolyte, are explained by considering the competitive hydration between ions and agar macromolecules. The effect of different cations on the α -value for tracer-diffusion is also explained using the same concept.

In Section B of this chapter, a study of the effect of gel concentration on the activation energy for

the diffusion process in different systems shows that (1) the activation energy decreases with increasing gel percentage (w) and it varies linearly with $w^{1/3}$, (2) the D_0 value also decreases with increasing gel percentage and shows a linear relationship with $w^{-2/3}$. These observations are explained on the basis of the transition state theory of diffusion.

The study of effect of the supporting electrolyte on the activation energy for the tracer-diffusion process shows that the activation energy for tracer-diffusion of Zn^{2+} and Mn^{2+} ions in different chlorides decreases in the following order :

(1) for tracer-diffusion of Zn^{2+} ions



(2) for tracer-diffusion of Mn^{2+} ions



while the trend in activation energy for the tracer-diffusion of Mn^{2+} ions in different transition metal sulphates shows the following order :



The observed trend in the activation energy in different systems is explained qualitatively in terms of charge density of the ions and the distortion caused by them in the gel-water structure.