Diffusion Studies of Some Zinc Salts in Gel Medium

S.F. Patil, N.S. Rajurkar, A.V. Borhade and Munmun Nath

Department of Chemistry, University of Poona, PUNE - 411 007

Mutual-diffusion of some of the zinc salts is studied over a concentration range of 1 X 10^{-6} - 0.5 mol dm^{-3} using 1% agar gel medium at 25°C by zone-diffusion technique. Comparing experimental values with the values computed on the basis of Onsager-Fuoss theory of diffusion, a deviation is observed. The non-agreement of the experimental with the theoretical values is explained on the basis of various interactions taking place in the ion-gel-water system. It is observed that obstruction effect in the diffusion of zinc salts at a given concentration decreases with increasing charge density of the anion of the salt. This observation is accounted for on the basis of competitive hydration between ions and agar macromolecules. Finally activation energy for mutual-diffusion of different electrolytes at a concentration of 0.1 mol dm^{-3} is determined by least square fitting of the diffusion coefficient data obtained at various temperatures. The decrease in activation energy with increase in charge density of the anions is explained by considering the extent of distortion caused in the gel water system.

After the development of mathematical theory for mutual diffusion by Onsager and Fuoss [1], numerous studies have been carried out by several workers [2-6] to see its applicability to different electrolytes. Most of the data available in literature is for alkali metal salts. Work on transition metal salts is limited. There are only few reports [7-11] on the measurement of activation energy for the process of diffusion because of the experimental difficulties encountered in the measurement of diffusion coefficient at higher temperatures.

Agar gel, by virtue of its strucutre, is capable of holding about 98% water in practically immobilized and semi-rigid state, eliminating the direct streaming convectional flow of solution and provides an ideal medium for the study of diffusion at higher temperatures. The present paper reports the measurement of diffusion coefficients of $Zn(NO_3)_2$, $ZnBr_2$ and ZnI_2 at various concentrations in 1% agar gel medium to examine the applicability of Onsager-Fuoss theory to these systems, to determine the obstruction effect of the gel and activation energy for the process of diffusion at a concentration of 0.1 mol dm^{-3}.

EXPERIMENTAL

Agar (Difco, bacto-agar, Detroit, Michigan, USA) was used to prepare gel. Diffusion coefficient of various zinc salts (AR grade) were measured in agar gel medium. Zone-diffusion technique was used for determining the values of mutual-diffusion coefficients, the details of which are given in an earlier paper [12]. A radioisotope, ^{65}Zn (BARC, Bombay, India) with $t_{1/2}$ = 244 d, was used to label the solution. The concentration of the electrolytes was varied between 10^{-6} to 0.5 mol dm^{-3}.

Obstruction effect in the systems chosen (0.1 mol dm^{-3}) was investigated by varying gel concentration between 1 - 2.5% at 25°C while activation energy was determined by varying the temperature between 25-40°C in 1% agar gel. The values of diffusion coefficients reported are an average of four independent measurements with a precision of ± 0.5%.

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RESULT AND DISCUSSION

Concentration dependence

Values of mutual diffusion coefficient as a function of concentration is presented in Fig. 1. Theoretical values are calculated using the Onsager - Fuoss equation [1]. Taking into account the activity coefficient (a thermodynamic term) and electrophoretic factor (a kinetic term), Onsager and Fuoss [1] arrived at the following expression:

$$D = 1000\ RT\ (\nu_1+\nu_2)\ \frac{\overline{M}}{D}\ \left(1 + C\frac{\delta \ln y_{\pm}}{\delta C}\right) \quad ...(1)$$

The various symbols have their usual meaning. Here $\overline{M}/C$ is the electrophoretic term and $(1 + C\ \delta \ln y_{\pm}/\ \delta C)$ is the thermodynamic term and are computed using various expressions described earlier [13].

After substituting various parameters controlling the diffusion process in eq (1), the following expressions for theoretical mutual diffusion coefficients of the zinc salts are obtained:

$$D_{\text{Zinc nitrate}} = 7.4327 \times 10^{13} \times \left[16.3038 - \frac{4.8757\sqrt{C}}{1 + 1.9021\sqrt{C}} + 139.060\ C + 1.9021\sqrt{C}\right] 10^{-20} \left[1 - \frac{2.0308\sqrt{C}}{(1 + 1.9021\sqrt{C})^2} + 0.3488\ C\right] \quad .... (2)$$

$$D_{\text{Zinc bromide}} = 7.4327 \times 10^{13} \times \left[16.9229 - \frac{5.799\sqrt{C}}{1 + 3.1430\sqrt{C}} + 145.8229\ C + 3.1430\sqrt{C}\right] 10^{-20} \left[1 - \frac{2.0306\sqrt{C}}{(1 + 3.1430\sqrt{C})^2} + 0.0926\ C\right] \quad .... (3)$$

$$D_{\text{Zinc iodide}} = 7.4327 \times 10^{13} \times \left[16.8068 - \frac{5.6187\sqrt{C}}{1 + 4.0647\sqrt{C}} + 144.543\ C + 4.0647\sqrt{C}\right] 10^{-20} \left[1 - \frac{2.0306\sqrt{C}}{(1 + 4.0647\sqrt{C})^2} + 0.4901\ C\right] \quad .... (4)$$

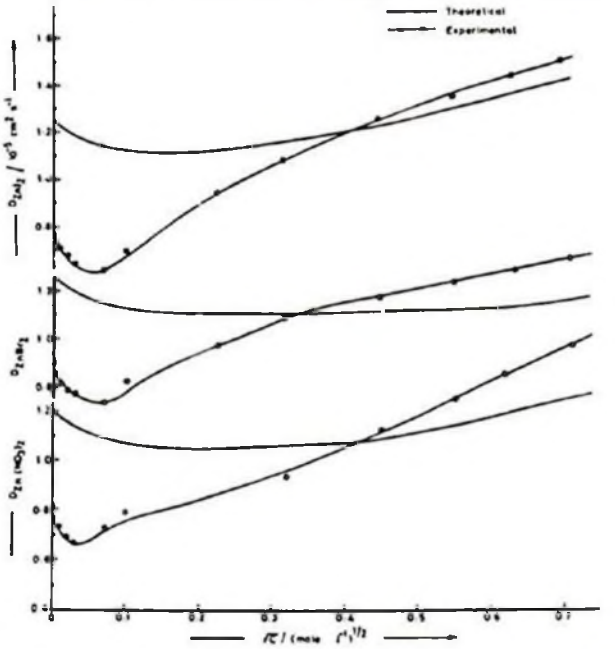


Fig. 1 Variation of Mutual diffusion coefficients with concentration in 1% agar gel at 25°C.

The values of theoretical diffusion coefficients at different concentration were calculated using equations 2 - 4 and shown graphically along with the experimental values in Fig. 1. Examination of the Fig. reveals that the experimental values of diffusion coefficients are always less than the theoretical ones at lower concentrations and exceeds the theoretical values at higher concentrations. One more interesting feature to be noted is that D_{theo} $vs\ \sqrt{C}$ plot shows a rounded and not a sharp minimum, whereas D_{expt} $vs\sqrt{C}$ plot shows a sharp minimum. Further these are found to be at lower concentration side than the theoretical ones. Theoretical minima occur at 0.1 mol dm^{-3} for both $Zn(NO_3)_2$ and $ZnBr_2$ systems and at 5 X 10^{-2} mol dm^{-3} for ZnI_2 system; experimental minima for $Zn(NO_3)_2$ occurs at 1 X 10^{-3} mol dm^{-3} and for $ZnBr_2$ and ZnI_2 occur at 5 X 10^{-3} mol dm^{-3} concentration.

The observed results can be explained qualitatively by considering different types of interactions occurring in the ion-gel-water system. The various effects which play an important role in determining the experimental values of diffusion coefficients are:

(1) adsorption effect resulting from cation exchange capacity of agar gel,

(2) obstruction effect caused by the macromolecules of agar,

(3) water-gel interaction due to binding of water molecules in the fibres of agar,

(4) ion water interaction and

(5) ion-ion interactions, governed by coulombic and field dielectric gradient forces [14] (which are important at higher concentrations).

Former two effects cause lowering of diffusion coefficients while the latter three interactions are responsible for the enhancement in the diffusion rate. The observed lower values of diffusion coefficients in the concentration range of 10^{-6} to 0.1 mol dm^{-3} indicate that the adsorption and obstruction effects dominate over the water gel interaction. On the other hand, the values of mutual-diffusion coefficients at higher concentrations are higher than the theoretical ones, showing that the diffusion enhancing interactions dominate over adsorption and obstruction effects under these conditions.

According to Onsager-Fuoss theory, a minimum in D *vs* $\sqrt{C}$ plot occurs due to the positive salting constant of an electrolyte in the thermodynamic term. At lower concentrations, the contribution of the term containing salting constant B in the expression for thermodynamic term is negligible, while the second term with negative sign dominates and hence thermodyamic term decreases giving an overall decreasing trend in D_{theo} values with concentration of electrolyte. At higher concentrations, the term containing B dominates and is responsible for the upward trend in the theoretical diffusion coefficient values beyond the minimum. Further, the shift in the minimum towards the lower concentration side in D_{expt} *vs* $\sqrt{C}$ curves is accounted for on the basis of ion-ion interactions and changes in hydration of ions with concentration of electrolyte which were not considered by Onsager-fuoss in their theoretical treatment.

Obstruction Effect

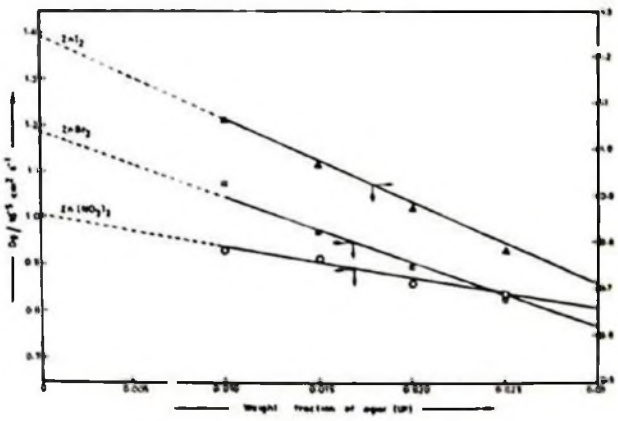


Fig. 2 Obstruction effect in the diffusion of $Zn(NO_3)_2$, $ZnBr_2$ and ZnI_2 at 0.1 M electrolyte concentration at 25°C.

The variation in mutual diffusion coefficient with weight fraction of agar (ω) (Fig 2) for various systems studied obeys the following relation [15,16]:

$$D_g = D_a - a\omega \qquad ...(5)$$

where D_g is the diffusion coefficient in the gel medium, D_a is the value of D_g extrapolated to zero agar content and a is the slope of the plot of D_g *vs* ω.

The values of obstruction effect ($\alpha = a/D_a$) in various systems are recorded in Table 1. The extent of hydration of agar (H), in terms of grams of bound water per gram of anhydrous agar is estimated using Wang's [8] equation

$$\alpha = [1/d_a + H/d_w]\, d_w \quad (\beta \cdot 1) \quad \ldots\ldots (6)$$

where d_a and d_w are the densities of anhydrous agar (1.6) and water (1.0) respectively and β is the shape factor for agar molecules (5/3 for needle shape). The values of H are also included in the Table.

Table 1

α and H-values for the electrolyte diffusion in agar gel

Electrolyte: $Zn(NO_3)_2$/ $ZnBr_2$ / ZnI_2 in agar gel 0.1 mol. dm^{-3}

Temp : 25°C.

Electrolyte	α value	H-value
$Zn(NO_3)_2$	6.80	9.58
$ZnBr_2$	12.06	17.46
ZnI_2	14.86	21.67

The values of α follow the trend

$$Zn(NO_3)_2 < ZnBr_2 < ZnI_2$$

This trend is explained on the basis of competitive hydration between ions and agar molecules in a diffusion medium.

The extent of hydration of agar is affected in the presence of different ions because of the varying abilities of the ions to attract the water molecules. When we consider a system containing both ions and agar molecules, there will be competition between them for hydration. If hydration of agar is studied with common cation, its extent would depend on the nature of anions. Anion, NO_3^-, with ionic radius 1.65 Å [17] has a higher charge density and is capable of attracting more water molecules and this results in lower obstruction value. Br^- and I^- with ionic radii 1.95 and 2.16 Å [18] respectively have lower charge densities and hence the higher obstruction values in $ZnBr_2$ and ZnI_2.

Activation Energy

Activation energies for mutual-diffusion of $Zn(NO_3)_2$, $ZnBr_2$ and ZnI_2 at 0.1 mol dm^{-3} concentration in 1% agar gel are determined by the least square fitting of the diffusion coefficient data through Arrhenius plots (Fig.3) and are presented in Table 2.

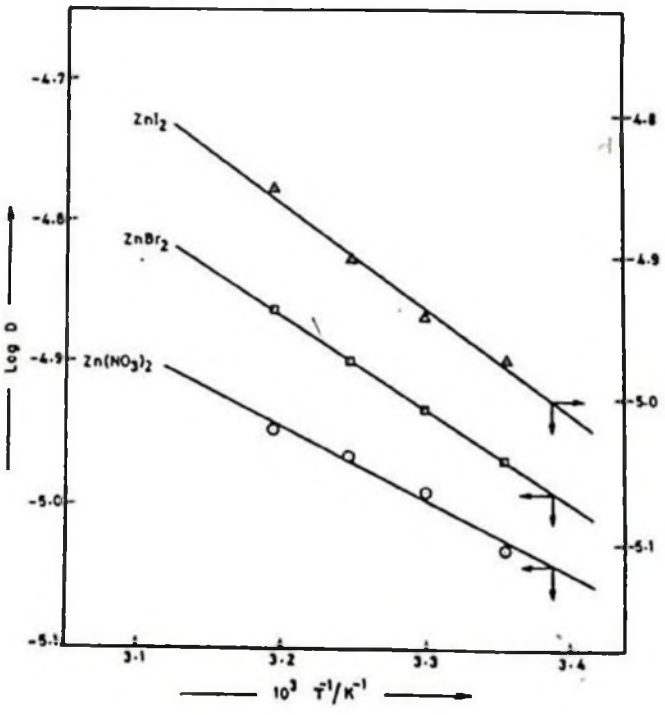


Fig. 3 Arrhenius plots for the diffusion of $Zn(NO_3)_2$, $ZnBr_2$ and ZnI_2 in 1% agar gel at 0.1 M of the electrolyte.

Table 2

Activation energy (E in kJ mol^{-1}) for electrolyte diffusion

Electrolyte concentration : 0.1 mol dm^{-3}.
Agar concentration: 1 %

Electrolyte	Ionic radii of anions (Å)	E/kJ mol^{-1}
$Zn(NO_3)_2$	1.65	9.7 ± 0.9
$ZnBr_2$	1.95	12.8 ± 0.9
ZnI_2	2.16	14.4 ± 0.6

As can be seen from Table 2, the activation energy increases as the charge density of the anion decreases. This can be explained as follows: During the formation of gel, the water molecules are trapped in the fibres of agar gel network by hydrogen bonds [19], adsorption [20] and dipole-dipole interaction [21]. This results in a loose water structure throughout the gel. In presence of electrolytes in the gel, ions hold the water molecules more firmly than agar molecules and thus immobilized water melts and the gel-water structure loosens. The cations being common in the present systems studied, the extent of melting of gel should depend on the charge density of the anions. As has been discussed earlier, ions with higher charge density attract more water dipoles and hence melt the gel-water structure to a larger extent. The distortion caused in the short range crystalline structure of water due to local gel melting increases the self-energy of the ions thereby decreasing the energy barrier for the process of diffusion. From this picture, it can be inferred that the activation energy required for the diffusion in different electrolytes should be in the reverse order to the charge density of anion of the electrolytes. Thus, the energy of activation for diffusion process should be the least in the medium containing NO_3^- ions (having highest charge density among the anions studied). It should be the highest in the medium containing I^- ions. The observed results are in agreement with the above concept.

REFERENCES

1. L. Onsager and R.M. Fuoss, *J.Phys.Chem.*, **36** (1932) 2689.
2. H.S. Harned and R.M. Hudson, *J.Am.Chem.Soc.*, **73** (1951) 5083.
3. G.J. Jang, B.C. Oliver, B.R. Lakshminarayan and G.E. Mayer, *J. Phys. Chem.*, **74** (1970) 1285.
4. R.A. Robinson and C.L. Chia, *J.Am.Chem.Soc.* **74** (1952) 2776.
5. P.J. Reilly and R.H. Stokes, *Aust.J.Chem.*, **24** (1971) 1361.
6. V. Luk, L. Nanis and M.Litt, *Ind. Congr. Chem. Fundam.* **14** (1975) 92.
7. S.F. Patil and N.G. Adhyapak, *Int. J.Appl. Radiat. Isot.*, **32** (1981) 631.
8. J.H. Wang, *J.Am.Chem.Soc.*, **76** (1954) 4755.
9. B.K. Pathak, P.C. Singh and V.N. Singh, *Acta Cienc. Ind.*, **4** (1981) 231.
10. K.N. Han and T.K. Kang, *Metallurgical Transaction B*, **17B** (1986) 425.
11. S.F. Patil, N.S. Rajurkar and A.V. Borhade, *J. Radioanal. Nucl. Chem.*, **173** (1993) 153.
12. H.J. Arnikar, S.F. Patil, N.G. Adhyapak and J.K. Potdar, *Z.Phys.Chem.*, **120** (1980) 51.
13. S.F. Patil, N.G. Adhyapak and S.N. Patel, *J. Radioanal Nucl. Chem. Lett.*, **96** (1985) 87.
14. W.B. Lowell, *J.Phys.Chem.*, **76** (1972) 1062.
15. A.L. Slade, A.C. Cremers and H.C. Thomas, *J.Phys.Chem.* **70** (1966). 2840.
16. A.G. Langdon and H.C. Thoms, *J.Phys.Chem.*, **75** (1971) 1821.
17. H.D.B. Jenkins and K.P. Thakur, *J.Chem.Educ.*, **56** (1979) 576.
18. N.A. Lange, *Handbook of Chemistry*, 4th Edn., **(Handbook publishers, INC. Sandusku, Ohio)**, (1941). 57.
19. B. Jirgensons and M.B. Straamanis, *A Short Text Book of Colliod Chemistry*, **Pergamon Press Ltd., London**, (1945).
20. V.N. Felicetta, A.E. Mrkhum, Q.P. Peniston and J.L. McArthy, *J.Am.Chem.Soc.*, **71** (1948) 2879.
21. S.A. Gilman and I.G. Shuhtsova, *Kolloid Z.*, **21** (1958) 25.