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Diffusivity of Zinc Ions in Aqueous Alkali-Metal Chlorides

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The tracer-diffusion coefficients of radioactive zinc ions in aqueous potassium chloride, cesium chloride, and lithium chloride solutions of concentration between 0.005 and 2.5 mol dm^{-3} are determined using an open-ended capillary technique with stirring. The theoretical tracer-diffusion coefficients of zinc ions in aqueous salt solutions are calculated using the Gosting−Harned equation and compared with the experimentally determined diffusion coefficients. The measured values of tracer-diffusion coefficients of zinc ions in the aqueous alkali-metal chloride solutions agree with the theoretically predicted values up to a concentration of about 0.05 mol dm^{-3}. At higher concentrations, the tracer-diffusion coefficient of zinc ions first increases and again decreases with concentration, giving rise to a maximum in the plot of the tracer-diffusion coefficient against the square root of the concentration. A qualitative explanation of the concentration dependence of the tracer-diffusion coefficient of zinc ions in concentrated solutions of the salts is attempted by taking into account the ion−ion and ion−water interactions.

Introduction

In engineering practice, the diffusion coefficient enters into important parameters for mass transport correlations such as the Schmidt and Sherwood numbers. The importance of diffusion coefficients in electrochemical engineering is associated directly with the limiting current density of electrode reactions.

A survey of the literature shows that diffusion of alkali-metal ions (*1−3*) has been extensively studied using various techniques, both in gel medium and in aqueous solutions. However, only limited data are available on the diffusion of transition-metal ions. The self-diffusion coefficients of some transition-metal ions (Co^{2+}, Mn^{2+}, and Zn^{2+}) in aqueous solution (*4*, *5*) at various concentrations have been reported earlier from our laboratory. The aim of the present work is to determine tracer-diffusion coefficients of Zn^{2+} ions in alkali-metal chlorides KCl, CsCl, and LiCl over a wide range of concentration using the open-ended capillary technique with stirring and to see the applicability of Onsager's theory (*6*) and Wang's (*7*) model of diffusion to these systems.

Experimental Section

Tracer-diffusion coefficients of Zn^{2+} ions labeled with ^{65}Zn ($t_{1/2}$ = 244 d) in KCl, CsCl, and LiCl were determined at 25 °C over the concentration range of 0.005−2.5 mol dm^{-3}. ^{65}Zn isotope was obtained from the Board of Radiation and Isotope Technology (Unit of Department of Atomic Energy, Government of India) while AR grade KCl, CsCl, and LiCl were from Central Drug House (P) Ltd., Bombay. The initial concentration of ^{65}Zn in tracer solution was calculated to be 6.66×10^{-6} mol dm^{-3} on the basis of the activity provided by the BRIT. This solution was diluted 10^5 times before use in diffusion experiments. Tracer-diffusion coefficients were measured using an open-ended capillary technique, the experimental setup being the same as that of Wang (*7*). Flat-bottomed capillaries with an internal diameter of 1.0 mm and length of 1.0 cm were used for the measurement of tracer-diffusion coefficients. The tracer solution in capillaries was prepared by labeling the same concentration of the chloride salt as present in the diffusion bath with $^{65}Zn^{2+}$ ions. The capillaries, after being filled with desired labeled solution, were fixed in a perspex stand and held vertically in the diffusion apparatus consisting of a 1 L three-necked flask. After attainment of thermal equilibrium, the capillaries were gradually lowered in the diffusion bath. A possible source of error with this technique is due to convection disturbances at the top of the capillary. Two effects can be distinguished, both of them tending to sweep out a part of the active solution of the capillary and leading, therefore, to effective diffusion paths shorter than the geometric length of the capillary. These are (1) an immersion effect (ΔD) resulting from the immersion of the capillary into inactive solution and (2) a Δl effect which occurs due to stirring of the inactive solution in order to maintain the boundary condition at the mouth of the capillary. In the present study we have reduced both these effects to a minimum. The immersion effect is minimized by using the capillaries with one end ground flat and square and the other ground to a taper to reduce the disturbances caused by immersion. This effect was further minimized by keeping a large drop of inactive solution of the same concentration on the top of the capillary through which diffusion takes place. ΔD was estimated as described by Krauss and Spinks (*8*), by allowing the diffusion to proceed for 1 min. ΔD was found to be only 0.3%. The second source of error, the scooping effect due to the stirring, was reduced to a minimum by adjusting the stirring speed. The diffusion apparatus was provided with a two-pan glass stirrer, and a stirring speed of 90 revolutions min^{-1} was maintained throughout the diffusion run using a stepper motor drive. Antivibrating rubber sheets were used to reduce other mechanical disturbances in the thermostat. The diffusion was allowed to proceed for a period of 25 h. The concentration of the Zn^{2+} ions was analyzed in terms of radioactivities of the solution in the capillary, before and after the diffusion run. The radioactivity of the solution was measured using a single channel analyzer with a NaI (Tl) detector. Other technical details have been described in an earlier paper (*1*).

The average concentration of solution in the capillary after diffusion run time t is given by

$$\frac{c_{av}}{c_o} = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp[-(2n+1)^2\pi^2 Dt/4l^2] \qquad (1)$$

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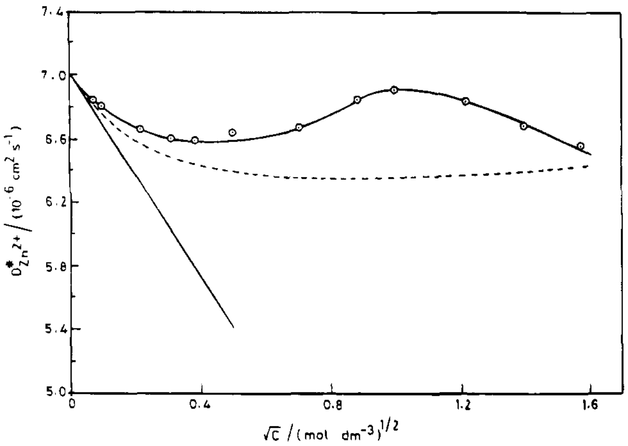

Figure 1. Variation of the diffusion coefficient of zinc ions with the concentration of KCl at 25 °C: (—) limiting law, (- - -) extended limiting law, (⊙) experimental data.

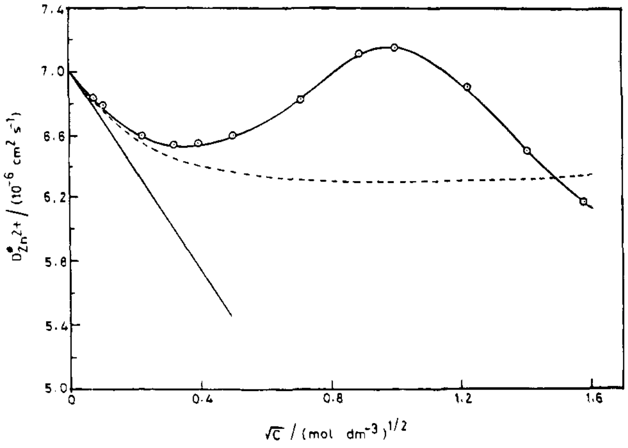

Figure 2. Variation of the diffusion coefficient of zinc ions with the concentration of CsCl at 25 °C: (—) limiting law, (- - -) extended limiting law, (⊙) experimental data.

Table 1. Values of Various Parameters Involved in Calculation of Theoretical Diffusion Coefficients of Zn^{2+} Ions in Various Supporting Electrolytes

	supporting electrolyte		
parameter	KCl	CsCl	LiCl
$\lvert Z_1\rvert$	2	2	2
$\lvert Z_2\rvert$	1	1	1
$\lvert Z_3\rvert$	1	1	1
$\lambda_1°$/(S mol^{-1} cm^2)	105.6	105.6	105.6
$\lambda_2°$/(S mol^{-1} cm^2)	73.5	77.26	38.64
$\lambda_3°$/(S mol^{-1} cm^2)	76.35	76.35	76.35
$d\omega_j$	0.739	0.744	0.669
A'	1.421	1.290	1.331

where c_{av} is the average concentration of the tracer ion in the capillary after diffusion, c_o is the initial concentration of the tracer ion in the capillary, D is the diffusion coefficient, t is the time of diffusion, and l is the length of the capillary. n takes the values from 0 to ∞.

When the value of Dt/l^2 is greater than 0.2, which was always the case in the present work, the series on the right-hand side of eq 1 converges so rapidly that all terms following the first can be neglected. Thus, eq 1 can be written in the form

$$Dt/l^2 = 4/\pi^2 \ln(8c_o/\pi^2 c_{av}) \qquad (2)$$

but c_o/c_{av} can be taken to be equal to a_o/a_{av}. Here a_o is the initial radioactivity of the diffusant, and a_{av} is the radioactivity of the diffusant after diffusion time t. Hence, eq 2 may be written as

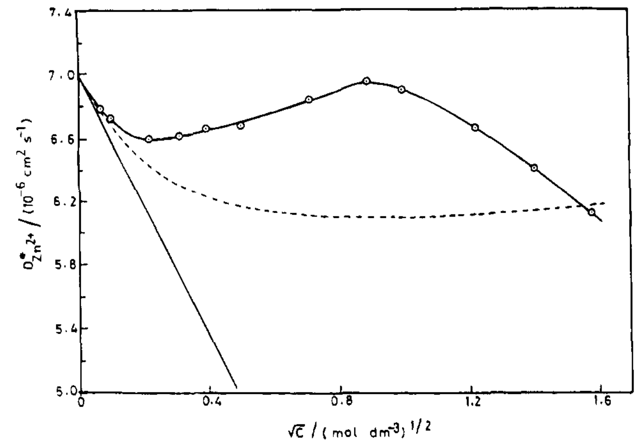

Figure 3. Variation of the diffusion coefficient of zinc ions with the concentration of LiCl at 25 °C: (—) limiting law, (- - -) extended limiting law, (⊙) experimental data.

$$Dt/l^2 = (4/\pi^2) \ln(8a_o/\pi^2 a_{av}) \qquad (3)$$

Equation 3 was used to calculate the experimental tracer-diffusion coefficients from the measured value of a_o/a_{av} in the present work. Each value of D^*_{expt} reported is the mean of four completely separate experiments with a precision of ±1%. In order to check the accuracy of the method, the self-diffusion coefficients of I^- ions in 0.1 and 0.01 mol dm^{-3} KI solutions were measured in our laboratory (*4*) using ^{131}I isotope and were found to be in close agreement with an accuracy of ±1.7% within experimental uncertainty with those reported by Mills and Kennedy (*9*) using the same technique. The temperature of the thermostat was maintained at 25 °C throughout the experiment with a variation of ±0.1 °C.

Results and Discussion

Diffusion coefficients are calculated on the basis of the Onsager theory (*6*) and compared with experiment. The equation derived by Gosting and Harned (*10*) and used in subsequent calculations is given below:

$$D^*_j = \frac{RT\lambda_j°}{|Z_j|F^2} - \frac{\lambda_j°|Z_j|F}{3N\epsilon}(2.694 \times 10^{16})\left(\frac{4\pi}{\epsilon RT}\right)^{1/2} [1 - (d\omega_j)^{1/2}](\sum_i c_i Z_i^2)^{1/2} \qquad (4)$$

Here D_j^* is the tracer-diffusion coefficient of an ion j, R the gas constant, F the Faraday constant, N the Avogadro number, ϵ the dielectric constant of the medium, $\lambda_j°$ the equivalent conductance of the diffusing ion j, with charge Z_j, c the concentration of the ions, and $d\omega_j$ the mobility term which is an involved function of charge (Z), equivalent conductance (λ), and concentration (c) of ions in the diffusion medium and is given by the equation

$$d\omega_j = \frac{1}{\sum c_i Z_i^2} \sum_i \frac{c_i|Z_i|\lambda_i°}{\frac{\lambda_i°}{|Z_i|} + \frac{\lambda_j°}{|Z_j|}}$$

Various parameters required for the theoretical calculation of the diffusion coefficients are given in Table 1. Substituting these parameters in eq 4, the following

Table 2. Variation of the Tracer-Diffusion Coefficient D^* of Zinc Ions with the Concentration of Supporting Electrolyte at 25 °C

	$D^*_{Zn^{2+}}/(10^{-6}\ cm^2\ s^{-1})$		
$c/(mol\ dm^{-3})$	KCl	LiCl	CsCl
5×10^{-3}	6.8421	6.7801	6.8412
1×10^{-2}	6.8092	6.7224	6.7892
5×10^{-2}	6.6663	6.6009	6.5893
0.1	6.6109	6.6213	6.5401
0.15	6.5982	6.6607	6.5443
0.25	6.6414	6.6814	6.6076
0.5	6.7995	6.8419	6.8234
0.8	6.8443	6.9513	7.1228
1.0	6.9231	6.9012	7.1792
1.5	6.8398	6.6711	6.9017
2.0	6.6808	6.4104	6.5003
2.5	6.5610	6.1089	6.1805

limiting law expressions are obtained for different supporting electrolytes:

$$D^*_{Zn^{2+}}/(10^{-6}\ cm^2\ s^{-1}) = 7.0239 - 3.2110(c/c_0)^{1/2} \quad \text{in KCl} \quad (5)$$

$$D^*_{Zn^{2+}}/(10^{-6}\ cm^2\ s^{-1}) = 7.0239 - 3.1491(c/c_0)^{1/2} \quad \text{in CsCl} \quad (6)$$

$$D^*_{Zn^{2+}}/(10^{-6}\ cm^2\ s^{-1}) = 7.0239 - 4.1826(c/c_0)^{1/2} \quad \text{in LiCl} \quad (7)$$

where $c_0 = 1.0$ mol dm^{-3}.

However, at higher concentrations an empirical correction made by Stokes *et al.* (*11*) is introduced; the corresponding equations for KCl, CsCl, and LiCl, respectively (extended limiting law expressions), are

$$D^*_{Zn^{2+}}/(10^{-6}\ cm^2\ s^{-1}) = 7.0239 - \frac{3.2110(c/c_0)^{1/2}}{(1 + 1.421(c/c_0)^{1/2})(1 + 1.421((c/c_0)/2)^{1/2})} \quad (8)$$

$$D^*_{Zn^{2+}}/(10^{-6}\ cm^2\ s^{-1}) = 7.0239 - \frac{3.1491(c/c_0)^{1/2}}{(1 + 1.290(c/c_0)^{1/2})(1 + 1.290((c/c_0)/2)^{1/2})} \quad (9)$$

$$D^*_{Zn^{2+}}/(10^{-6}\ cm^2\ s^{-1}) = 7.0239 - \frac{4.1826(c/c_0)^{1/2}}{(1 + 1.331(c/c_0)^{1/2})(1 + 1.331((c/c_0)/2)^{1/2})} \quad (10)$$

Theoretical diffusion coefficients along with the corresponding experimental values as a function of electrolyte concentration for the tracer diffusion of Zn^{2+} ions in KCl, CsCl, and LiCl systems are shown in Figures 1−3. The experimental curves have been plotted by hand through the points obtained. Experimental values of the diffusion coefficients are also presented in Table 2.

Examination of Figures 1−3 (Table 2) shows that, at the very low concentrations studied, the experimental values of diffusion coefficients for all the systems agree well with the theoretical ones. At concentrations higher than 0.05 mol dm^{-3} for LiCl, higher than 0.1 mol dm^{-3} for CsCl, and higher than 0.15 mol dm^{-3} for KCl, diffusion coefficients of Zn^{2+} ions start to increase with the concentration of the electrolytes, reaching a maximum at 0.8 mol dm^{-3} for LiCl and at 1.0 mol dm^{-3} for the KCl and CsCl systems. With a further increase in the concentration of the electrolytes the diffusion coefficients decrease, showing a quantitative breakdown of the Onsager theory (*6*) at higher concentrations.

The trend in the diffusion coefficient can be explained on the basis of Wang's model (*7*) which takes into consideration changes in the physical properties occurring at the microscopic level. The increase in the diffusion coefficient beyond a certain concentration is attributed to changes in the local relative permittivity as a result of increased ion−ion interactions leading to a reduction in the total energy barrier for diffusion at higher concentrations.

At still higher concentrations, the tracer-diffusion coefficients again start to decrease with increasing salt concentration. This is because at these high concentrations the relaxation effect eventually dominates the effect of an increase of self-energy. Further, at higher concentrations the main diffusing species may not be just Zn^{2+} ions which may exist as chloro complexes such as $ZnCl^+$, $ZnCl_2$, and $Zn(ZnCl_4)$ (*12*) or higher negatively charged species which are expected to have a lower diffusing rate. Hence, the diffusion coefficients again decrease with concentration as observed.

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