

# Diffusivity of Some Zinc and Cobalt Salts in Water

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The diffusion coefficients of  $Zn(NO_3)_2$ ,  $ZnBr_2$ , and  $CoSO_4$  in water have been measured by using  $^{65}Zn$  ( $t_{1/2} = 244$  d) and  $^{60}Co$  ( $t_{1/2} = 5.27$  y) as tracers with an improved open-ended capillary technique at 25 °C which is rapid and does not involve stirring. Nanis' analytical solution for the nonstirring mode is used for computation of the diffusion coefficients over a wide range of concentrations ( $10^{-6}$ –0.5 M). The measured diffusion coefficients are compared with the theoretical results estimated from the Onsager–Fuoss theory. The deviation between theoretical and experimental values has been attributed to ion–ion interactions and other factors which were not considered in the Onsager–Fuoss theory.

## Introduction

There are several methods (1–6) for measuring the diffusion coefficients in the solution state, among which the capillary method (7) is most universally adaptable. In order to maintain a zero boundary condition at the mouth of the capillary, stirring of the solution in the bath is necessary. But this leads to scooping the solution from the capillary, resulting in shortening of the effective diffusion path (the  $\Delta l$  effect) which results in a high value of diffusion coefficients. A solution to this problem is to avoid stirring.

A computer simulation of the diffusion process without stirring provides a procedure for the estimation of diffusion coefficients from a residual amount in the capillary. If stirring is not provided in an actual experiment, then the  $D$  values computed using an equation that accounts for stirring (zero boundary condition) would clearly be less than the true value.

Nanis *et al.* (8) gave an analytical solution, using the Laplace transform method and putting no restriction on the capillary mouth concentration. The simplified equation is given in the Experimental Section.

Diffusion of monovalent salts has been extensively studied using the capillary technique, while studies on the diffusion of transition-metal salts are limited. The present paper deals with the determination of diffusion coefficients of some zinc and cobalt salts in water at 25 °C over a concentration range of  $1 \times 10^{-6}$  to 0.5 M with a view to verify the applicability of the Onsager–Fuoss theory for these systems.

## Experimental Section

Pyrex glass capillaries of length 38 mm and a uniform diameter (inner diameter 1.2 mm and outer diameter 7 mm) were used for the study. In each diffusion measurement four capillaries were filled with the desired concentration of the solution using a microliter syringe. These capillaries were then fixed in a perspex stand and lowered very gradually into a beaker of 1-L capacity containing pure distilled water, allowing the diffusion process to proceed. The beaker containing pure water and the capillaries was itself completely immersed in the thermostat maintained at  $25 \pm 0.1$  °C. The details of the capillary technique are reported in our earlier paper (9), and Nanis' analytical solution (8) used for computation of  $D$  is

$$a/a_0 = 1 - (Dt/\pi l^2)^{1/2} \quad (1)$$

where  $a$  is the activity of the diffusant after diffusion time  $t$ ,  $a_0$  the initial activity of the diffusant,  $D$  the diffusion coefficient of the electrolyte, and  $l$  the length of the capillary.

Table I. Variation of  $D_{Zn(NO_3)_2}$  with the Concentration of the Electrolyte in Water at 25 °C

C/(mol L <sup>-1</sup> )	$D_{Zn(NO_3)_2}/$ (10 <sup>-5</sup> cm <sup>2</sup> s <sup>-1</sup> )		C/(mol L <sup>-1</sup> )	$D_{Zn(NO_3)_2}/$ (10 <sup>-5</sup> cm <sup>2</sup> s <sup>-1</sup> )	
	theor	expt		theor	expt
$1 \times 10^{-6}$	1.2021	1.1800	$1 \times 10^{-2}$	1.0703	1.0412
$1 \times 10^{-5}$	1.1915	1.1712	0.10	1.0503	1.0616
$1 \times 10^{-4}$	1.1828	1.1551	0.20	1.0943	1.1018
$5 \times 10^{-4}$	1.1527	1.1201	0.30	1.1550	1.1701
$1 \times 10^{-3}$	1.1508	1.1100	0.40	1.1937	1.2352
$5 \times 10^{-3}$	1.1037	1.0623	0.50	1.2609	1.2890

$^{65}Zn$  and  $^{60}Co$  were used as tracers for the measurements of electrolyte diffusion coefficients of  $Zn(NO_3)_2$ ,  $ZnBr_2$ , and  $CoSO_4$ . The time of diffusion was kept at 4 h.

The experimental diffusion coefficient values reported are the average of four independent measurements with a precision of  $\pm 1\%$ .

## Results and Discussion

The equations derived from the Onsager–Fuoss (10) theory and used for calculating theoretical diffusion coefficient values are

$$D = 1000RT(\nu_1 + \nu_2) \left( \frac{\bar{M}}{C} \right) \left( 1 + C \frac{\partial \ln y_{\pm}}{\partial C} \right) \quad (2)$$

where  $\bar{M}/C$  is the electrophoretic term and is given by

$$\frac{\bar{M}}{C} = 1.074 \times 10^{-20} \frac{\lambda_1^{\circ} \lambda_2^{\circ}}{|Z_1||Z_2|\Lambda^{\circ}} + \frac{\Delta m'}{C} + \frac{\Delta m''}{C} \quad (3)$$

$$\frac{\Delta m'}{C} = \frac{-(|Z_2|\lambda_1^{\circ} - |Z_1|\lambda_2^{\circ})^2}{\Lambda^{\circ 2}|Z_1||Z_2|(\nu_1 + \nu_2)} \frac{3.11 \times 10^{-19}}{\eta_0(\epsilon T)^{1/2}} \frac{\Gamma^{1/2}}{1 + A'C^{1/2}} \quad (4)$$

$$\frac{\Delta m''}{C} = \frac{(Z_2^2 \lambda_1^{\circ} + Z_1^2 \lambda_2^{\circ})^2}{\Lambda^{\circ 2}} \frac{9.18 \times 10^{-13}}{\eta_0(\epsilon T)^2} C \phi A' C^{1/2} \quad (5)$$

$1 + C(\partial \ln y_{\pm}/\partial C)$  is the thermodynamic term and is given by

$$1 + C \frac{\partial \ln y_{\pm}}{\partial C} = 1 - \frac{1.1514 S_f C^{1/2}}{(1 + A'C^{1/2})^2} + 4.606 BC \quad (6)$$

$\nu_1$  and  $\nu_2$  are the number of cations and anions in the electrolyte,  $T$  is the absolute temperature,  $C$  is the concentration,  $Z_1$  and  $Z_2$  are the valences of the cation and the anion respectively,  $\eta_0$  is the viscosity of the medium,  $y_{\pm}$  is the mean activity coefficient,  $A'C^{1/2}$  is the exponential integral function

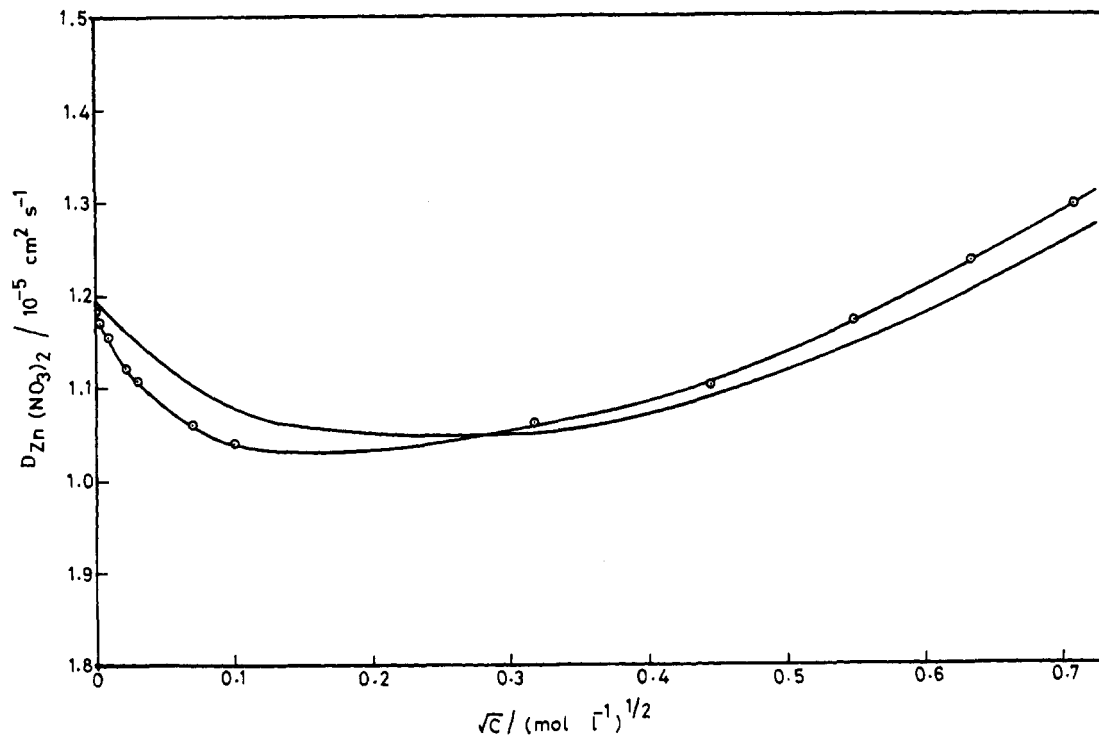


Figure 1. Variation of  $D_{\text{Zn}(\text{NO}_3)_2}$  in pure water with the square root of the concentration of the electrolyte at 25 °C: (—) theoretical, (○) experimental.

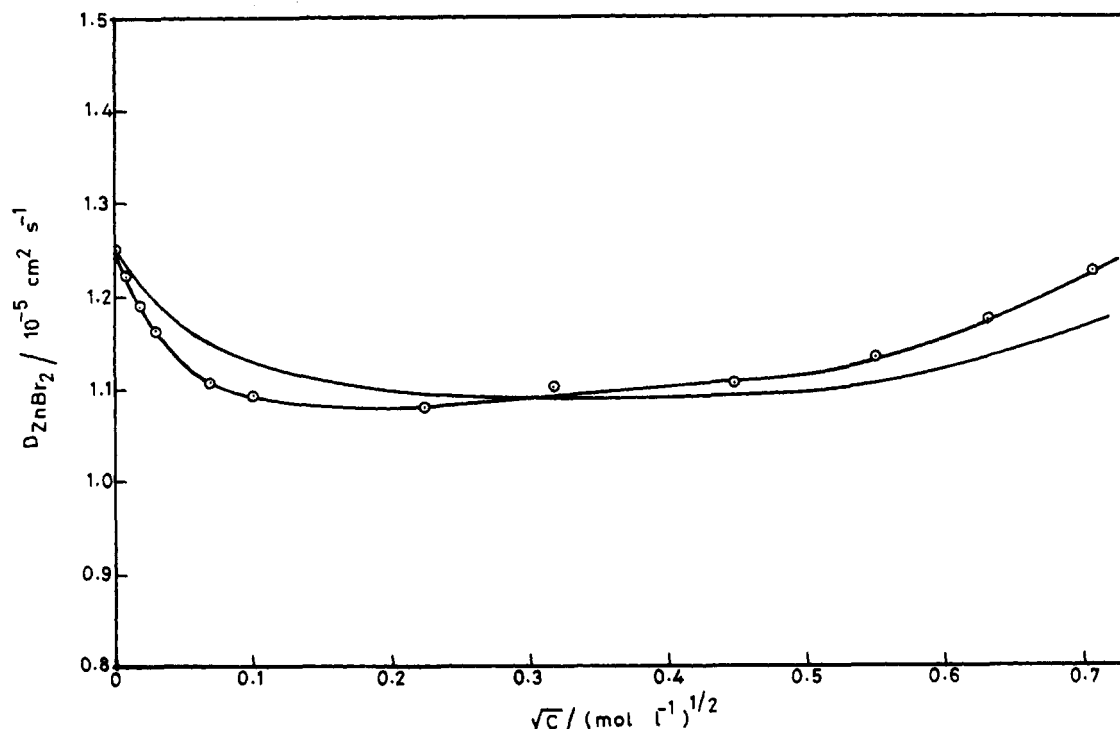


Figure 2. Variation of  $D_{\text{ZnBr}_2}$  in pure water with the square root of the concentration of the electrolyte at 25 °C: (—) theoretical, (○) experimental.

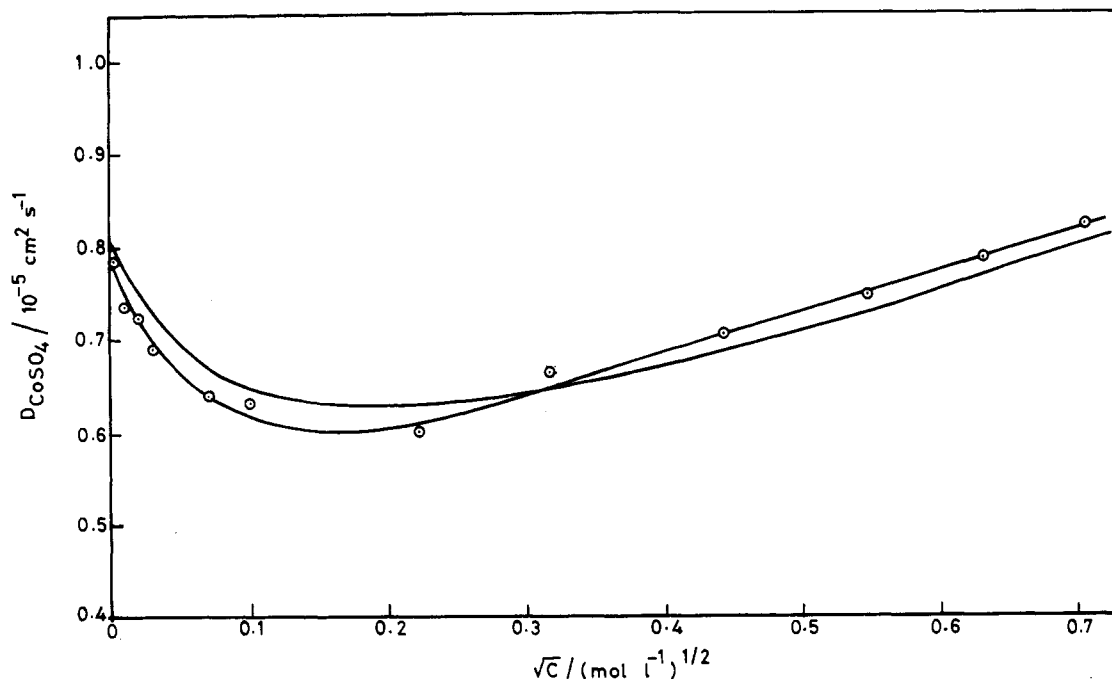
of the theory,  $S_f$  is the limiting slope of the Debye-Hückel theory,  $B$  is the salting constant,  $A'$  is a constant given by  $ka/C^{1/2}$  where  $k$  is the Debye-Hückel reciprocal radius, and  $a$  is the distance of closest approach between opposite ions.

The experimental diffusion coefficient values calculated using eq 1 along with the theoretically computed values are presented in Tables I-III, and as a function of the square root of the concentration in Figures 1-3.

For the lower concentration range (<0.1 M), the experimental values of the diffusion coefficients are less than the

theoretical values. At very low concentrations, the deviation is small and the experimental values approach the Nernst limiting value. At higher concentrations, however, the experimental values of diffusion coefficients exceed the theoretical values.

At lower concentrations the difference may be due to incomplete dissociation or complex formation of the salts. At higher concentrations, however, the retarding effect of incomplete dissociation or complex formation on the rate of diffusion is probably compensated by ion-ion interactions.



**Figure 3.** Variation of  $D_{\text{CoSO}_4}$  in pure water with the square root of the concentration of the electrolyte at 25 °C: (—) theoretical, (○) experimental.

**Table II.** Variation of  $D_{\text{ZnBr}_2}$  with the Concentration of the Electrolyte in Water at 25 °C

$C/(\text{mol L}^{-1})$	$D_{\text{ZnBr}_2}/(10^{-5} \text{ cm}^2 \text{ s}^{-1})$		$C/(\text{mol L}^{-1})$	$D_{\text{ZnBr}_2}/(10^{-5} \text{ cm}^2 \text{ s}^{-1})$	
	theor	expt		theor	expt
$1 \times 10^{-6}$	1.2549	1.2507	$5 \times 10^{-2}$	1.0928	1.0798
$1 \times 10^{-5}$	1.2489	1.2399	0.10	1.0918	1.1027
$1 \times 10^{-4}$	1.2321	1.2187	0.20	1.1035	1.1295
$5 \times 10^{-4}$	1.2076	1.1908	0.30	1.1182	1.1492
$1 \times 10^{-3}$	1.1921	1.1635	0.40	1.1317	1.1705
$5 \times 10^{-3}$	1.1474	1.1077	0.50	1.1487	1.2387
$1 \times 10^{-2}$	1.1267	1.0918			

**Table III.** Variation of  $D_{\text{CoSO}_4}$  with the Concentration of the Electrolyte in Water at 25 °C

$C/(\text{mol L}^{-1})$	$D_{\text{CoSO}_4}/(10^{-5} \text{ cm}^2 \text{ s}^{-1})$		$C/(\text{mol L}^{-1})$	$D_{\text{CoSO}_4}/(10^{-5} \text{ cm}^2 \text{ s}^{-1})$	
	theor	expt		theor	expt
$1 \times 10^{-6}$	0.8047	0.8011	$5 \times 10^{-2}$	0.6304	0.6000
$1 \times 10^{-5}$	0.7970	0.7872	0.10	0.6477	0.6621
$1 \times 10^{-4}$	0.7756	0.7380	0.20	0.6893	0.7051
$5 \times 10^{-4}$	0.7446	0.7261	0.30	0.7283	0.7452
$1 \times 10^{-3}$	0.7234	0.6901	0.40	0.7662	0.7851
$5 \times 10^{-3}$	0.6722	0.6402	0.50	0.8011	0.8209
$1 \times 10^{-2}$	0.6498	0.6380			

These interactions enhance the diffusion rate, resulting in higher diffusion coefficient values than the theoretical ones. These factors have not been considered by the Onsager–Fuoss theory. Such deviations have also been reported earlier by some researchers (11–14). Though deviations are observed from the theory, the general trend in the variation of experimental diffusion coefficients with the square root of the concentration obtained for  $\text{Zn}(\text{NO}_3)_2$ ,  $\text{ZnBr}_2$ , and  $\text{CoSO}_4$  systems is in agreement with the Onsager–Fuoss theory.

In Figures 1–3 minima are present in the  $D$  vs  $C^{1/2}$  plots for both theory and experiment for  $\text{Zn}(\text{NO}_3)_2$ ,  $\text{ZnBr}_2$ , and  $\text{CoSO}_4$ . The minima observed in the theoretical curves are attributed to the contribution of the thermodynamic term in the Onsager–Fuoss theory of diffusion coefficients (eq 6). At low concentrations the second term of eq 6 has a negative sign and leads to a decrease in the diffusion coefficient values with an increase in concentration. At higher concentrations, the third term, containing the salting constant  $B$ , predominates and leads to an increase in the  $D$  values with concentration, leading to the minimum in the  $D$  vs  $C^{1/2}$  curve as observed in all the systems studied.

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