

## TRACER-DIFFUSION OF $\text{Co}^{2+}$ IONS IN SOME TRANSITION METAL CHLORIDE SOLUTIONS

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Tracer-diffusion coefficients of  $\text{Co}^{2+}$  ions have been determined in 1% agar gel containing transition metal chlorides, viz.  $\text{ZnCl}_2$ ,  $\text{NiCl}_2$  and  $\text{MnCl}_2$  over the concentration range of  $10^{-6}$ –0.15M at 25 °C using the zone-diffusion technique. The results are compared with calculated values on the basis of Onsager's theory and the deviations are accounted for on the basis of various types of interactions in the ion-gel water system. Further, activation energy for the tracer-diffusion of  $\text{Co}^{2+}$  ions in the above mentioned electrolytes has been obtained as a function of electrolyte concentration, using measurements in the temperature range of 25–50 °C. The trend in activation energy is explained on the basis of the WANG's model.

In a series of publications from this laboratory, we have reported the diffusion coefficients of  $\text{Co}^{2+}$  ions in alkali metal chlorides,<sup>1,2</sup> nitrates<sup>3</sup> and transition metal sulfates<sup>4</sup> under different experimental conditions. The present work extends the diffusion studies to transition metal chlorides. Diffusion coefficients of  $\text{Co}^{2+}$  ions in different transition metal chlorides in 1% agar gel at 25 °C as well as energy of activation for the diffusion of  $\text{Co}^{2+}$  ions in these electrolytes at different concentrations are reported.

### Experimental

In the first set of experiments, diffusion coefficients of  $\text{Co}^{2+}$  ions labeled with  $^{60}\text{Co}$  (5.27 y) have been determined in 1% agar gel containing  $\text{ZnCl}_2$ ,  $\text{MnCl}_2$  and  $\text{NiCl}_2$  over the concentration range of  $10^{-6}$ –0.15M at 25 °C. The second set of experiments deals with the measurement of activation energy for diffusion of  $\text{Co}^{2+}$  ions in these electrolytes. For this purpose diffusion coefficients of  $\text{Co}^{2+}$  ions in different transition metal chlorides were measured by varying the temperature between 25–50 °C and electrolyte concentration between  $10^{-5}$ –0.1M, the gel concentration being 1%. The zone-diffusion technique was used for the determination of diffusion coefficient, the details of which were described earlier.<sup>5</sup>

### Results and discussion

The ONSAGER-GOSTING-HARNED<sup>6,7</sup> equation for tracer-diffusion of an ion is:

$$D_j^* = \frac{RT\lambda_j^0}{|Z_j|F^2} - \frac{\lambda_j^0|Z_j|F}{3Ne} \cdot 2.694 \cdot 10^{16} \sqrt{\frac{4\pi}{eRT}} \times \times [1 - \sqrt{d_{(w)}}] \sqrt{\sum_i C_i Z_i^2} \quad (1)$$

where  $d_{(w)}$  is the mobility term which is a complicated function of charge and equivalent conductance of the ions from the diffusion medium and other symbols have their usual meaning, the values of the various parameters<sup>8</sup> being reported in Table 1.

Table 1  
Values of various parameters for the calculation of tracer-diffusion coefficients of  $\text{Co}^{2+}$  ions in different supporting electrolytes

Parameter	Supporting electrolyte		
	MnCl <sub>2</sub>	ZnCl <sub>2</sub>	NiCl <sub>2</sub>
Z <sub>1</sub>	2	2	2
Z <sub>2</sub>	2	2	2
Z <sub>3</sub>	1	1	1
$\lambda_1^0/S \text{ cm}^2 \cdot \text{gm}^{-1}$	49	49	49
$\lambda_2^0/S \text{ cm}^2 \cdot \text{gm}^{-1}$	53.5	52.8	54
$\lambda_3^0/S \text{ cm}^2 \cdot \text{gm}^{-1}$	76.35	76.35	76.35
$d_{(w)}$	0.6003	0.5981	0.6018
A'	2.701	2.887	2.682

Substitution of these values in Eq. (1) leads to the following limiting law expressions for the systems studied

$$D_{\text{Co}^{2+}}^*/10^{-6} \text{ cm}^2 \cdot \text{s}^{-1} = 6.518 - 7.964 \sqrt{C} \quad \text{in MnCl}_2 \quad (2)$$

$$D_{\text{Co}^{2+}}^*/10^{-6} \text{ cm}^2 \cdot \text{s}^{-1} = 6.518 - 8.014 \sqrt{C} \quad \text{in ZnCl}_2 \quad (3)$$

$$D_{\text{Co}^{2+}}^*/10^{-6} \text{ cm}^2 \cdot \text{s}^{-1} = 6.518 - 7.929 \sqrt{C} \quad \text{in NiCl}_2 \quad (4)$$

while the corresponding extended limiting law expression, obtained by replacing  $\sqrt{C}$  by  $\sqrt{C}/(1 + A'\sqrt{C}) (1 + A'\sqrt{C}/\sqrt{2})^2$ , where  $A' = ka/\sqrt{C}$ , and  $k$  is the reciprocal radius of the ion/atmosphere,  $a$  the closest distance of approach between opposite ions, are

$$D_{\text{Co}^{2+}}^*/10^{-6} \text{ cm}^2 \cdot \text{s}^{-1} =$$

$$= 6.518 - 7.964 \frac{\sqrt{C}}{(1 + 2.701\sqrt{C})(1 + 2.701\sqrt{C}/\sqrt{2})} \quad \text{MnCl}_2 \quad (5)$$

$$D_{\text{Co}^{2+}}^*/10^{-6} \text{ cm}^2 \cdot \text{s}^{-1} =$$

$$= 6.518 - 8.014 \frac{\sqrt{C}}{(1 + 2.887\sqrt{C})(1 + 2.887\sqrt{C}/\sqrt{2})} \quad \text{ZnCl}_2 \quad (6)$$

$$D_{\text{Co}^{2+}}^*/10^{-6} \text{ cm}^2 \cdot \text{s}^{-1} =$$

$$= 6.518 - 7.929 \frac{\sqrt{C}}{(1 + 2.682\sqrt{C})(1 + 2.682\sqrt{C}/\sqrt{2})} \quad \text{NiCl}_2 \quad (7)$$

The values of  $D_{\text{Co}^{2+}}^*$  calculated by the above equations are plotted as a function of  $\sqrt{C}$  in Figs 1-3, ( $\text{MnCl}_2$ ), ( $\text{ZnCl}_2$ ) and ( $\text{NiCl}_2$ ), respectively. These figures also show the experimental values.

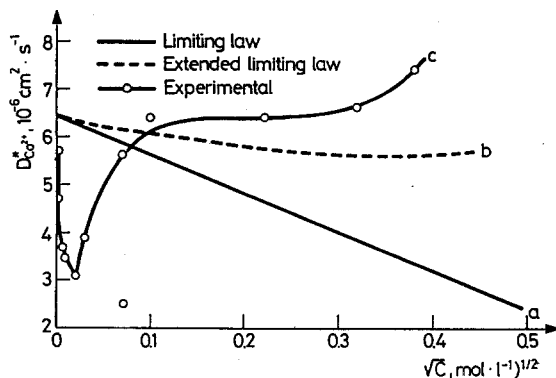


Fig. 1. Variation of  $D_{\text{Co}^{2+}}^*$  with the square root of manganese chloride concentration in 1% agar gel at 25 °C

A glance at Figs 1-3 indicates that the experimental values are always less than the theoretical ones in the lower concentration range (up to  $5 \cdot 10^{-3}\text{M}$  in case of  $\text{MnCl}_2$ ,  $\text{NiCl}_2$  and  $5 \cdot 10^{-2}\text{M}$  in case of  $\text{ZnCl}_2$ ), while a reverse trend is observed at higher

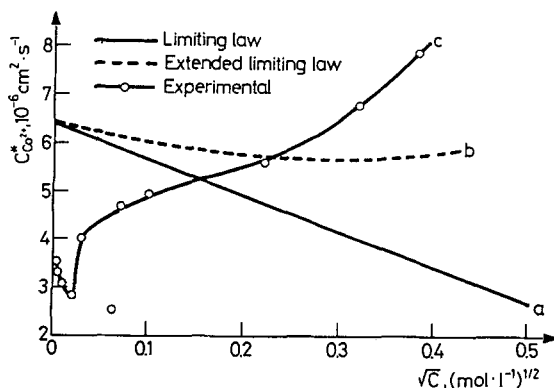


Fig. 2. Variation of  $D_{\text{Co}^{2+}}^*$  with the square root of zinc chloride concentration in 1% agar gel at 25 °C

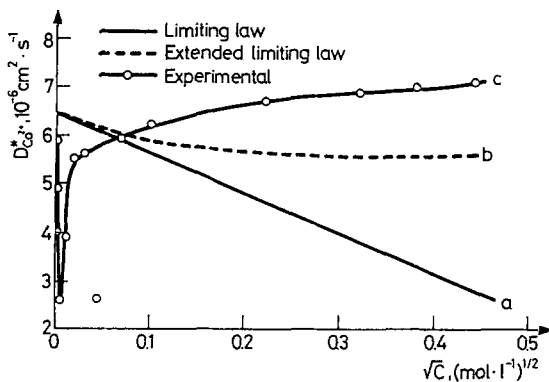


Fig. 3. Variation of  $D_{\text{Co}^{2+}}^*$  with the square root of nickel chloride concentration in 1% agar gel at 25 °C

concentrations. Further examination of these figures shows that the experimental values of the diffusion coefficient decrease with increase of electrolyte concentration in agreement with the theory. But after certain concentration it increases, giving rise to a minimum ( $5 \cdot 10^{-4}\text{M}$  –  $\text{MnCl}_2$ ,  $\text{ZnCl}_2$  and  $5 \cdot 10^{-5}\text{M}$  –  $\text{NiCl}_2$ ), while there is no minimum in the theoretical curve. These deviations over the entire concentration range are attributed to various effects in the ion-gel-water system viz. diffusion retarding relaxation, adsorption and obstruction effects, and diffusion enhancing gel-water, ion-water and ion-ion interactions. These effects have been described in earlier papers.<sup>10,11</sup>

A comparison of the diffusion coefficients in various transition metal chlorides shows that the theoretical diffusion coefficients of  $\text{Co}^{2+}$  ions calculated on the basis of

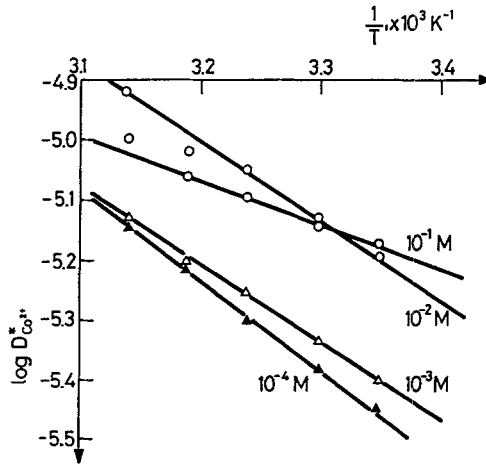


Fig. 4. Activation energy for tracer-diffusion of  $\text{Co}^{2+}$  ions in  $\text{MnCl}_2$  as a function of electrolyte concentration in 1% agar gel

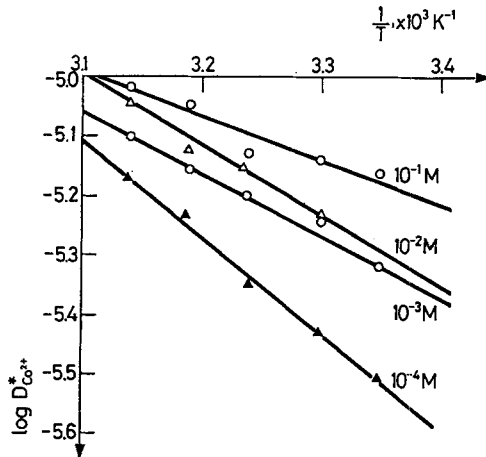


Fig. 5. Activation energy for tracer-diffusion of  $\text{Co}^{2+}$  ions in  $\text{ZnCl}_2$  as a function of electrolyte concentration in 1% agar gel

the limiting law are in the order



while that calculated on the basis of extended limiting law shows that  $D_{\text{theo}}^*$  is the highest in  $\text{ZnCl}_2$ , while it is of the same order in nickel and manganese chlorides.

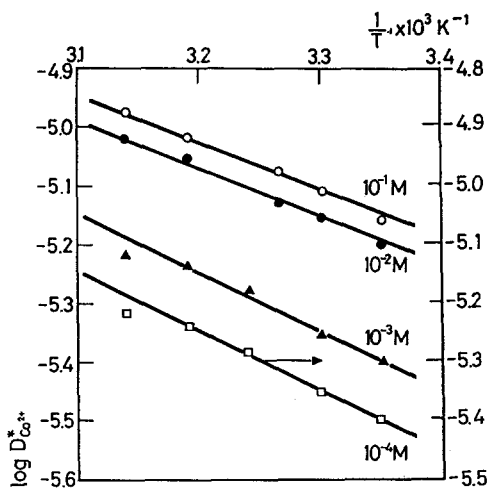


Fig. 6. Activation energy for tracer-diffusion of  $\text{Co}^{2+}$  ions in  $\text{NiCl}_2$  as a function of electrolyte concentration in 1% agar gel

Table 2  
Activation energy for the diffusion of  $\text{Co}^{2+}$  ions in different supporting electrolytes

Concentration, M	E, $\text{kJ} \cdot \text{mol}^{-1}$
$\text{NiCl}_2$	
$10^{-5}$	$19.85 \pm 0.5$
$10^{-3}$	$18.68 \pm 0.7$
$10^{-2}$	$16.47 \pm 0.9$
$10^{-1}$	$15.54 \pm 0.6$
$\text{ZnCl}_2$	
$10^{-4}$	$31.90 \pm 0.9$
$10^{-3}$	$22.25 \pm 0.5$
$10^{-2}$	$18.71 \pm 0.7$
$10^{-1}$	$16.41 \pm 0.5$
$\text{MnCl}_2$	
$10^{-4}$	$32.8 \pm 0.9$
$10^{-3}$	$24.25 \pm 0.9$
$10^{-2}$	$22.05 \pm 0.9$
$10^{-1}$	$17.61 \pm 0.6$

However, there is no definite trend in  $D_{\text{expt}}^*$  in any of these electrolytes and it varies with concentration. This fact indicates that the degree of various interactions which determines the overall  $D_{\text{expt}}^*$  value depends on the nature of ions in the medium as well as on its concentration.

The minimum in  $D_{\text{expt}}^*$  vs.  $\sqrt{C}$  curve can be reasonably explained qualitatively on the basis of WANG'S<sup>12</sup> model, which takes into consideration the changes in the physical properties occurring at the microscopic level with electrolyte concentration. The results can also be interpreted in terms of structure breaking properties of the ions affecting the sizes of ion-water aggregates by decoupling of hydrogen bonds.<sup>13</sup>

The Arrhenius plots for the tracer-diffusion of  $\text{Co}^{2+}$  ions in  $\text{MnCl}_2$ ,  $\text{ZnCl}_2$  and  $\text{NiCl}_2$  at various concentrations are presented in Figs 4, 5 and 6, respectively. The activation energies calculated by least-squares fitting of the data from these plots to the Arrhenius equation are listed in Table 2.

It is seen from Table 2 that in a given system, the activation energy decreases with increasing concentration of the electrolyte, in agreement with previous reports from this laboratory. The trend is explained qualitatively on the basis of WANG'S<sup>12</sup> model. As the concentration of the electrolyte increases, the distance between two ions decreases and it becomes increasingly difficult for water molecules to maintain the semicrystalline structure of water. The semicrystalline structure of water is thus broken up and the local dielectric constant of the medium increases, leading to an increase in the energy of ions in the normal state, while the energy of the activated state remains constant. Thus a decrease in the energy barrier of diffusion with increasing electrolyte concentration is observed.

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