Electrolyte diffusion of cobalt and manganese salts in water

S F Patil*, N S Rajurkar & A V Borhade
Department of Chemistry, University of Poona, Pune 411 007, India
Received 26 March 1993; revised and accepted 27 July 1993

Electrolyte diffusion coefficients of CoCl₂, Co(NO₃)₂, MnCl₂ and MnSO₄ in water have been measured using ⁶⁰⁰Co⁺ and ⁵⁴⁰⁰Mn⁺ as tracers with an open-ended, rapid improved capillary technique without stirring. Nanis analytical solution for non-stirring mode is used for computation of these electrolytes over a concentration range of 10⁻⁵-0.25 M at 25 ± 0.1°C. The measured diffusion coefficient values are compared with the theoretical values estimated on the basis of Onsager-Fuoss theory. The experimental diffusion coefficients agree reasonably well at low concentrations. The observed deviations between theoretical and experimental diffusion coefficients at high concentrations are attributed to the occurrence of ion-ion interactions which are not considered while formulating the Onsager-Fuoss theory.

In the previous papers from this laboratory we have applied a rapid, improved capillary technique without stirring developed by Nanis et al., for the computation of diffusion coefficients of ZnCl₂ (ref. 1), ZnBr₂, ZnI₂ and CoSO₄ (ref. 2) electrolytes. The present work is extended to salts of other transition metal ions, namely, CoCl₂, Co(NO₃)₂, MnCl₂ and MnSO₄ using the same technique with a view to examine the applicability of Onsager-Fuoss theory to diffusion of these salts.

Experimental

The diffusion coefficients of CoCl₂, Co(NO₃)₂, labelled with ⁶⁰⁰Co⁺ (t₁/₂ = 5.27 y) and of MnCl₂ and MnSO₄ labelled with ⁵⁴⁰⁰Mn⁺ (t₁/₂ = 312.2 d) were determined over the concentration range of 10⁻⁵-0.25 M in water using an improved open ended capillary method without stirring, the details of which are described in an earlier paper¹.

The length of the capillaries used was 36-38 mm with a uniform inner (1.3 mm) and outer (7 mm) diameters. These capillaries were filled with labelled electrolyte solution of interest having an activity of about 40,000 cpm measured on NaI (Tl) detector. The necessary precautions were taken to avoid introduction of any air bubble during filling of the capillary as well as to reduce immersion effect while lowering the capillary in water bath. The temperature of the thermostat containing the entire assembly was kept constant at 25 ± 0.1°C with a diffusion run time of 4 hrs.

The diffusion coefficient of electrolyte is then calculated using Eq. (1).

\[
\frac{C}{C₀} = 1 - \frac{D t^{1/2}}{\pi ² l} \quad \ldots \quad (1)
\]

where, \( C = \) activity of diffusant after diffusion, \( C₀ = \) initial activity of diffusant, \( D = \) diffusion coefficient \((\text{cm}^² \text{s}^{-1})\), \( l = \) length of the capillary \((\text{cm})\) and \( t = \) time allowed for diffusion \((\text{s})\).

It is to be noted that the experimental diffusion coefficient values calculated, using Eq. ·1 are an average of four independent measurements, with a precision of ± 1%.

Results and discussion

In order to check the validity of the Onsager-Fuoss theory for electrolyte-diffusion to the present systems studied, the theoretical diffusion coefficient values were calculated on the basis of this theory using Eq. (2)

\[
D' = \frac{1000 R T (ν₁ + ν₂)}{M/C} \left(1 + C \frac{∂ ln ν}{∂ C} \right) \quad \ldots \quad (2)
\]

where \( (M/C) \) is the electrophoretic term, \( (1 + C (∂ ln ν/∂ C)) \) is the thermodynamic term and other symbols have their usual meaning. The expressions for electrophoretic and thermodynamic terms are given in an earlier paper².

Substitution of various parameters in Eq. (1) leads to expressions (3-6) for the diffusion coefficients at 25°C.

\[
D_{\text{CoCl₂}} = 7.432 \times 10^{13} \left[ 16.027 - \frac{6.346 \sqrt{C}}{1 + 2.683 \sqrt{C}} + 149.67 C \phi 2.683 \sqrt{C} \right] \times 10^{-30} \left[ 1 - \frac{2.030 \sqrt{C}}{(1 + 2.683 \sqrt{C})^2} + 1.004 C \right] \quad \ldots \quad (3)
\]
The values of the theoretical diffusion coefficients computed by using Eqs 3-6 at various concentrations are shown in Figs 1-4 as a function of the square root of [electrolyte] along with the experimental values.

A comparison of the experimental and theoretical values of the diffusion coefficients for CoCl$_2$, Co(NO$_3$)$_2$, MnCl$_2$ and MnSO$_4$ shows that in the lower concentration range ($< 0.1$ M), experimental values of diffusion coefficients are less than the theoretical one. But at lowest concentration studied ($10^{-5}$ M) the deviation is quite small and the diffusion coefficient value approaches the Nernst limiting value.

![Graphs showing variation of diffusion coefficients with square root of concentration](image-url)

**Fig. 1**—Variation of $D'$ CoCl$_2$ with square root of [CoCl$_2$] in aq. solution at 25°C.

**Fig. 2**—Variation of $D'$ Co(NO$_3$)$_2$ with square root of [Co(NO$_3$)$_2$] in aq. solution at 25°C.

**Fig. 3**—Variation of $D'$ MnCl$_2$ with square root of [MnCl$_2$] in aq. solution at 25°C.

**Fig. 4**—Variation of $D'$ MnSO$_4$ with square root of [MnSO$_4$] in aq. solution at 25°C.
At the higher concentrations (> 0.1 \(M\)), however, experimental values are greater than the theoretical ones and the deviations are higher than those observed in the lower concentration range. Further, it is to be noted that theoretical and experimental minima in the \(D'\) versus \(\sqrt{C}\) plot are found to be identical for MnSO\(_4\) \((5 \times 10^{-2} M)\) system as well as for CoCl\(_2\) system \((1 \times 10^{-2} M)\). On the other hand, theoretical minimum in the diffusion plot for MnCl\(_2\) system is found to be at \(5 \times 10^{-2} M\) while the experimental minimum in the system is observed at \(1 \times 10^{-2} M\). Further, in the case of Co(NO\(_3\))\(_2\) system studied the experimental minimum is observed at \(5 \times 10^{-2} M\) but the theoretical minimum is found to be absent.

Though the theory of Onsager and Fuoss is highly successful for 1-1 electrolytes, there are many reports\(^5\)–\(^11\) in the literature in which it breaks down even for very dilute solutions of unsymmetrical electrolytes. Such deviations observed in the higher valence type of electrolytes are not surprising. One possible cause of this discrepancy was thought to be due to the inability of the theory to account for the behaviour of unsymmetrical polyvalent electrolytes as well as due to the incomplete dissociation and complex formation for such salts. The theoretical calculation involves only the mean mobilities of the ions and hence, a true computation of the theoretical value will require a knowledge of the degree of dissociation and mobilities of such ions as actually exist in the solution. Unfortunately these data are not available; therefore, it would be presumptuous to take too seriously the agreement between theory and experiment in the type of systems studied in the present work.

Further, though the Onsager-Fuoss theory is reasonably good for very dilute solutions, it cannot be expected to hold up to high concentrations as studied in the present work. At such high concentrations interaction between ions is dictated by both the coulombic and the field dielectric gradient forces\(^12\). These effects would cause the ions to continue a loose lattice configuration at such high concentrations. The Onsager-Fuoss theory does not address itself to these effects and hence would fail to explain results at high concentrations.

The presence of minimum in the \(D'\) versus \(\sqrt{C}\) plots in the systems studied can be explained in terms of the contribution of thermodynamic term of the Onsager-Fuoss theory towards the diffusion coefficient. At lower concentrations, the contribution of the positive term containing saltant B in the thermodynamic term\(^4\) is negligible, while the second term with negative sign dominates, leading to the decrease in thermodynamic term giving an overall decreasing trend in \(D'_{\text{theo}}\) with concentration of the electrolyte. However, at higher concentrations, the term containing saltant constant becomes important compared to the second one, thus thermodynamic term and hence the diffusion coefficient increases giving rise to a minimum in the \(D'\) versus \(\sqrt{C}\) curve.

However, in the case of Co(NO\(_3\))\(_2\) system the saltant constant is negative and hence the presence of minimum is not expected by the theory. The presence of minimum in the experimental curve observed in this system is attributed to the increase in activity coefficient due to effective desolvation of the ions because of ion-ion interactions in real solution.

Acknowledgement

One of us, (AVB) is thankful to CSIR, New Delhi for the award of senior research fellowship.

References