ELECTROLYTE—DIFFUSION OF CoSO₄ IN AQUEOUS SOLUTIONS

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ABSTRACT

Electrolyte–diffusion of $CoSO_4$ in pure aqueous solution is studied at 25 °C over a concentration range of 10^{-5}—0.25 mol/l. The measurement of diffusion coefficients are done by improved capillary technique without stirring. These values are compared with the theoretical values computed on the basis of Onsager–Fuoss theory.

Keywords: Diffusion coefficient   Onsager–Fuoss theory $CoSO_4$ Electrolyte diffusion

1   INTRODUCTION

In a series of papers from this laboratory we have reported the diffusion coefficients of various electrolytes[1-5] in agar gel medium and of Zn_2SO_4 in pure aqueous solution[6]. The present work was undertaken to see the applicability of the Onsager–Fuoss theory to electrolyte–diffusion of cobalt sulphate over a wide range of concentration in pure water at 25 ± 0.1 °C by the capillary technique without stirring[8,9].

2   EXPERIMENTAL

The diffusion coefficients of Co_2SO_4 labelled with ^{60}Co isotope ($t_{1/2}=5.27$ y) were determined over the concentration range of 10^{-5}— 0.25 mol/l in water using an improved rapid open ended capillary technique without stirring at 25 °C. For this purpose, a pyrex glass capillary of length 36— 38 mm and a uniform diameter (i.d. = 2.3 mm, o.d. = 7 mm), sealed at lower end, was filled with aqueous $CoSO_4$ solution of desired concentration using a medical syringe. The capillary was gradually lowered in a beaker containing water, after attainment of thermal equilibrium between solutions inside and outside the capillary. The entire assembly was itself completely immersed in a thermostat at the temperature 25 ± 0.1 °C. The immersion effect was avoided by placing a large drop of unlabelled solution of the same concentration before lowering the capillary. The duration of the diffusion run was about 4—5 h. The

activities of the solution before and after diffusion was measured using a single channel analyzer coupled to NaI(Tl) detector and the diffusion coefficients were calculated using the following equation:

$$C/C_o = 1 - (Dt/\pi l^2)^{1/2} \qquad (1)$$

where C and C_o are the activities of the diffusant after and before diffusion respectively, l is the length of the capillary and t is the time of diffusion. The accuracy of the results as evidenced by the multiple runs of the experiments is $\sim \pm 1\%$.

3 RESULTS AND DISCUSSION

The theoretical diffusion coefficients for CoSO₄ were calculated by using the following Onsager–Fuoss[7] equation:

$$D = 1000\, RT(v_1 + v_2)(\overline{M}/C)(1 + C\, \partial \ln y\pm /\partial C) \qquad (2)$$

where $(\overline{M}/C)$ and $(1 + C\partial \ln y\pm /\partial C)$ are the electrophoretic and thermodynamic terms respectively and other symbols have their usual meanings. The details for the computation of these terms are given in an earlier paper[1].

The incorporation of values of various parameters involved in the above mentioned equation leads to the following expression for CoSO₄ at 25 °C.

$$D_{CoSO_4} = 4.955 \times 10^{13} [16.318 - 2.474 C^{1/2}/(1 + 3.8266 C^{1/2})$$

$$+ 299.93 C \Phi 3.826 C^{1/2}] \times 10^{-20} \times [1 - 4.689 C^{1/2}/(1 + 3.826 C^{1/2})^2 + 0.3169 C] \qquad (3)$$

The values of theoretical diffusion coefficients computed by equation (3) are given in Table 1 along with the different terms involved in it as well as the experimental values obtained in the present work.

Table 1

Variation of D_{CoSO_4} with concentration of CoSO₄ in pure water at 25 °C

Conc. (mol/l)	$\overline{M}/C$ ($\times 10^{-20}$)	$1 + C(\partial \ln y\pm /\partial C)$	$D(\times 10^{-5} cm^2 s^{-1})$ Theo.	Exper.
0	—	—	0.808	—
1×10^{-5}	16.322	0.9855	0.798	0.787
5×10^{-5}	16.342	0.9686	0.784	0.750
1×10^{-4}	16.364	0.9565	0.775	0.738
5×10^{-4}	16.491	0.9112	0.744	0.726
1×10^{-4}	16.547	0.8823	0.725	0.690
5×10^{-4}	17.039	0.7962	0.672	0.610
1×10^{-2}	17.304	0.7579	0.649	0.535
5×10^{-2}	17.885	0.7113	0.630	0.525
1×10^{-1}	17.953	0.7281	0.648	0.672
0.15	17.982	0.7527	0.671	0.701
0.20	17.472	0.7781	0.674	0.738

A comparison of the experimental and theoretical values of the diffusion

coefficients shows that in the lower concentration range ($\leqslant 5 \times 10^{-2}$ mol/l) experimental values of diffusion coefficients are less than the theoretical one. But at lowest concentration studied, deviation is very small ($\sim 1.4\%$) and the diffusion value approaches Nernst limiting value at this concentration. At higher concentrations (> 0.1 mol/l), however, experimental values of the diffusion coefficients are greater than the theoretical one. But the deviations are less than those in the lower concentration range. This is due to the operation of ion–ion and ion–water interactions which tend to enhance the diffusion rate and are not considered by the theory. Further, it is to be noted that the magnitude of deviation for diffusion of Co_2SO_4 is less in pure water than in agar gel medium[5] and the observed minimum in the present work matches with that predicted by the theory and it occurs at 5×10^{-2} mol/l.

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