Diffusion Coefficient of Sodium Sulphate in Aqueous Solution at 45°

M. L. Soon*, G. KAUR & S. L. CHOPRA
Department of Chemistry, Punjab Agricultural University, Ludhiana 141 004

Received 21 August 1978; revised 7 February 1979; accepted 21 February 1979

The differential diffusion coefficients of sodium sulphate have been determined by the diaphragm cell technique at 45° in the concentration range 0.01-0.1 M. At these moderate concentrations, the results are not in accord with the Onsager-Fuoss theory.

The diffusion coefficients of potassium, magnesium, and beryllium sulphates have been determined in aqueous solutions with the help of a modified diaphragm cell having a completely new drive system devised in this laboratory. The differential diffusion coefficients of sodium sulphate in the concentration range 0.01-0.1 M have been determined and the data reported in this note.

In this investigation the use of the modified form of diffusion cell having a new drive system introduced in this laboratory was used. The iron sealed stirrers were provided to remove the stagnant layer of the liquid adhering to the surface of the diaphragm. A stirring rate of 56 r.p.m. was used throughout the experiments. The conductance of the solution in the upper compartment was measured at regular intervals of time by conductivity bridge (Yellow Spring Instrument Co., Ohio, USA, Model 31). The high vacuum stopcocks were all spring loaded. The volume of the pores of the diaphragm cell was determined as suggested elsewhere. After filling the diffusion cell as suggested by Sanni and Hutchison, the diffusion process was allowed to take place for one to three days until steady state condition was reached. Integral values of diffusion coefficients were then evaluated with the help of Eq. (1)

\[ \frac{\Delta C_f}{\Delta C_0} = \frac{\ln e}{t} \]  

where \( D, t, \Delta C_f \) and \( \Delta C_0 \) are the integral diffusion coefficient, cell constant, time (in seconds), final and initial concentrations of the solutions in the two compartments, respectively. The cell constant was determined in the usual manner and the value obtained was 0.1603. The constancy of the cell constant was checked twice during the present investigation. The integral values of diffusion coefficients obtained from Eq. (1) were next converted into the more fundamental \( D \) values using Eq. (2)

\[ D(C_m) = \frac{C_1 + C_3}{2} \]

where \( C_m = \frac{C_1 + C_3}{2} \) and \( C_m' = \frac{C_2 + C_4}{2} \)  

and

\[ D = D^0 + \frac{\sqrt{C}}{2} \frac{d D^0}{d \sqrt{C}} \]  

Plots of \( D \) vs \( \sqrt{C} \), \( D(C_m') \) vs \( \sqrt{C_m'} \), and \( D^0 \) vs \( \sqrt{C} \) are shown in Figs. 1, 2 and 3 respectively.

The theory of Onsager and Fuoss leads to the equation

\[ D = 1000RT\left( \frac{\gamma_1 + \gamma_2}{\gamma_1 + \gamma_2 + \gamma_3} \right) \left( 1 + C_{\text{m}} \right) \left( \frac{\ln e}{t} \right) \]  

where \( \gamma_1 \) and \( \gamma_2 \) are the number of ions that dissociate in the solution, \( \gamma_3 \) is the function given by (Eq. 6)

\[ \gamma_3 = \frac{Z_2^2 \left( \frac{Z_1 + Z_2}{Z_1 + Z_2} \right)}{3.132 \times 10^{-19} \left( \frac{Z_1 + Z_2}{Z_1 + Z_2} - 1 \right)^{1/2} \left( 1 + ka \right)} \]  

The plots of \( D \) vs \( \sqrt{C} \) and \( D(C_m') \) vs \( \sqrt{C_m'} \) are shown in Figs. 1 and 2 respectively.

\[ D = 1000RT\left( \frac{\gamma_1 + \gamma_2}{\gamma_1 + \gamma_2 + \gamma_3} \right) \left( 1 + C_{\text{m}} \right) \left( \frac{\ln e}{t} \right) \]  

where \( \gamma_1 \) and \( \gamma_2 \) are the number of ions that dissociate in the solution, \( \gamma_3 \) is the function given by (Eq. 6)

\[ \gamma_3 = \frac{Z_2^2 \left( \frac{Z_1 + Z_2}{Z_1 + Z_2} \right)}{3.132 \times 10^{-19} \left( \frac{Z_1 + Z_2}{Z_1 + Z_2} - 1 \right)^{1/2} \left( 1 + ka \right)} \]  

The plots of \( D \) vs \( \sqrt{C} \) and \( D(C_m') \) vs \( \sqrt{C_m'} \) are shown in Figs. 1 and 2 respectively.

\[ D = 1000RT\left( \frac{\gamma_1 + \gamma_2}{\gamma_1 + \gamma_2 + \gamma_3} \right) \left( 1 + C_{\text{m}} \right) \left( \frac{\ln e}{t} \right) \]  

where \( \gamma_1 \) and \( \gamma_2 \) are the number of ions that dissociate in the solution, \( \gamma_3 \) is the function given by (Eq. 6)

\[ \gamma_3 = \frac{Z_2^2 \left( \frac{Z_1 + Z_2}{Z_1 + Z_2} \right)}{3.132 \times 10^{-19} \left( \frac{Z_1 + Z_2}{Z_1 + Z_2} - 1 \right)^{1/2} \left( 1 + ka \right)} \]  

The plots of \( D \) vs \( \sqrt{C} \) and \( D(C_m') \) vs \( \sqrt{C_m'} \) are shown in Figs. 1 and 2 respectively.
In these equations, $D$ is the diffusion coefficient ($\text{cm}^2 \text{sec}^{-1}$), $T$ is the absolute temperature, $c$ is the concentration (mole per litre), $y_i$ is the activity coefficient on the molar concentration scale, $\epsilon$ is the dielectric constant of the water, and $\eta$ its viscosity. The equivalent conductances of the cation and anion are $\lambda_i$ and $\lambda_o$, respectively, and $\Lambda^o$ is their sum. $\epsilon \lambda_i \lambda_o$ is the limiting slope of the Debye and Hückel theory. $A'\sqrt{C} = A \sqrt{\epsilon}$ in which $\epsilon$ is the ionic concentration, $k$ is the reciprocal radius, $\lambda$ the mean distance of approach of the ions, and $A = 35.56 \times 1.01 / 2$. The quantity $a(ka)$ is the exponential integral function of the theory which may be obtained from tables given by Harned and Owen. $B$ is an empirical constant and $C \psi (d)$ the term required to convert the expression from rational into molar activity coefficient and is given by Eq. (10).

$$\psi (d) = \frac{(\partial \psi / \partial C + 0.001) (\gamma M_1 M_o)}{d + 0.001 C (\gamma M_1 M_o)} \ldots (10)$$

where

$$d = 0.9957 + 0.0479 c - 0.0023 c^{1/2}$$

and $M_1$ and $M_o$ are the molecular weights of the solvent and solute respectively.

The limiting value of the diffusion coefficient $D_0$ was obtained from Eq. (11).

$$D_0 = 8.936 \times 10^{-10} T \frac{\gamma_t + \gamma_a}{\gamma_t + 1} \frac{\lambda_t \lambda_o}{\lambda} \ldots (11)$$

In Table 1 the specific quantities used in the theoretical calculations are listed. Substitution of these data in Eqs. (5)-(9) leads to the numerical expression (12).

$$D = 7.934 \times 10^{13} \left(1 + C \frac{\partial \psi (d)}{\partial C}\right) \left(24.20 \times 10^{-20} + \frac{\Delta m'}{C} + \frac{\Delta m''}{C} \right) \ldots (12)$$

where

$$\Delta m = \left(\frac{Z_2 \lambda_t - Z_1 \lambda_o}{\Lambda} \right)^2 \frac{9.324 \times 10^{-13}}{\eta (e T)^2} C \phi (k a) \ldots (8)$$

The activity term $\left(1 + C \frac{\partial \psi (d)}{\partial C}\right)$ is represented by

$$1 + C \frac{\partial \psi (d)}{\partial C} = 1 - 1.1514 \frac{\Delta (\gamma M_1 M_o)}{(1 + \Lambda^{o} \sqrt{C})} + 2.303 BC - C \phi (d) \ldots (9)$$

Comparisons of the experimental results with those computed using Eqs. (12)-(15) are given in Table 2. In the last column values of $D' = D_{	ext{obs}} + (D - D_0)_{	ext{mea}}$ are recorded. The mean value of $D'(1.531)$ is not equal to the limiting value $D_0$. This confirmation of the inadequacy of the theory at concentrations up to 0.1 $M$ is in accord with similar agreement found for potassium$^{1,2}$, magnesium and beryllium sulphates$^8$. The variation in the diffusion coefficients may be attributed to surface effects (below 0.05 $M$) as suggested by Stokes$^9$ in addition to the effect of changing dielectric constant, changing viscosity of the medium and hydration etc. In Fig. 4, the observed and calculated diffusion coefficients have been plotted against the concentration. It is to be noted that the experimental values of diffusion coefficient of sodium sulphate are, however, obtained by the method of graphical integration as suggested by Stokes$^9$. The deviations between the experimental and calculated results can however, be narrowed by the use of a new correlation suggested earlier$^5$. 

---

**Table 2 — Calculated and Observed Diffusion Coefficients of Sodium Sulphate at 45°C**

<table>
<thead>
<tr>
<th>Conc. ($M$)</th>
<th>$10^6 D$ obs cm$^2$/sec</th>
<th>$10^6 D_{	ext{theo}}$ cm$^2$/sec</th>
<th>$10^6 D_0$ cm$^2$/sec</th>
<th>$10^6 D'$ cm$^2$/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>1.195</td>
<td>1.234</td>
<td>1.709</td>
<td>1.448</td>
</tr>
<tr>
<td>0.01</td>
<td>1.324</td>
<td>1.376</td>
<td>1.647</td>
<td>1.163</td>
</tr>
<tr>
<td>0.02</td>
<td>1.420</td>
<td>1.523</td>
<td>1.599</td>
<td>2.859</td>
</tr>
<tr>
<td>0.03</td>
<td>1.045</td>
<td>1.131</td>
<td>2.859</td>
<td></td>
</tr>
<tr>
<td>0.04</td>
<td>1.082</td>
<td>1.175</td>
<td>1.568</td>
<td>1.529</td>
</tr>
<tr>
<td>0.05</td>
<td>1.080</td>
<td>1.177</td>
<td>1.553</td>
<td>1.547</td>
</tr>
<tr>
<td>0.06</td>
<td>1.127</td>
<td>1.232</td>
<td>1.563</td>
<td>1.592</td>
</tr>
<tr>
<td>0.07</td>
<td>1.050</td>
<td>1.163</td>
<td>1.546</td>
<td>1.540</td>
</tr>
<tr>
<td>0.08</td>
<td>1.225</td>
<td>1.339</td>
<td>1.538</td>
<td>1.725</td>
</tr>
</tbody>
</table>

---

*Fig. 4—Plot of $D$ versus $C$ for Na$_2$SO$_4$ at 45°C [S.D. along X-axis = 0.001; and along Y-axis = 0.01 $\times 10^{-4}$]*
Metal Terphthalates & Dithioterphthalates & Their Complexes with Ethylenediamine

C. L. SHARMA*, T. K. DE & A. K. SINGH
Department of Chemistry, University of Roorkee, Roorkee 247 672

Received 28 October 1978; accepted 6 March 1979

Amperometric and conductometric titrations of terphthalic and dithioterphthalic acids with Cu(II), Ni(II) and Co(II) chlorides indicate the formation of 1 : 1 complexes, which have also been isolated in the solid form and characterised on the basis of analytical and IR data. The interaction of these compounds with ethylenediamine in benzene gives [Cu(en)]

_1

and [M(en)]

_3

where M = Co(II) or Ni(II) and t-terphthalate or dithioterphthalate. The thermal studies on metal terphthalates and dithioterphthalates have also been made.

Metal terphthalates have been studied in relation to their preparation by metathesis. The magnetic studies of only copper complexes of aliphatic and aromatic dicarboxylic (ortho substituted) acids are reported in the literature. The present note deals with the determination of composition and structure of Cu(II), Ni(II) and Co(II) complexes of terphthalic and dithioterphthalic acids using amperometric, conductometric, magnetic and IR studies. The results arrived at have been confirmed by chemical analysis, DTA, TG and DTG. The interaction of these compounds with ethylenediamine has also been studied.

Metal chlorides, terphthalic acid, ethylenediamine (en), benzene and sodium hydroxide were all AR (BDH) reagents. Dithioterphthalic acid was obtained from Evans Chemetics, USA. The solutions of acids were prepared in two equivalents of alkali and of others in doubly distilled water.

The solid complexes were prepared by adding equal volumes of 0.1 M of the reactants. The heavy precipitates formed were filtered, washed several times with distilled water and then dried in a desiccator over anhydrous sulphuric acid.

These compounds were treated with more than two equivalents of ethylenediamine in benzene and the mixture refluxed for 1 hr. The resulting complexes were filtered, washed several times with benzene and finally with absolute ethyl alcohol and then dried at ~80°C in an oven. The insolubility of the complexes in water and organic solvents precluded the measurement of molar conductance and molecular weight determinations.

The amperometric titrations carried out at -1.6, -1.8 and -0.6 V in the case of Cu(II), Ni(II) and Co(II) respectively indicated the formation of 1:1 complexes. This stoichiometry was also confirmed by conductometric titrations and chemical analysis of the isolated products (Table 1).

The ethylenediamine complexes are stable in solid state or in organic solvents but dissociate in water giving parent acids. The electronic spectra of the ethylenediamine complexes were found to be the same, indicating the formation of [Cu(en)]

_2

+ or [M(en)]

_2

where M = Co(II) or Ni(II), in solution and the acids in the form of precipitates.

The IR spectra (ν max in cm⁻¹) of metal terphthalates and of the acids indicated shift of ν C=O, ν C−O and ν C−O−ν O−C bands of the ligand appearing at ~1660, ~1410 and ~1270 to 1570, 1380 and 1140 respectively in the complexes;

TABLE 1—ANALYTICAL DATA AND MAGNETIC MOMENTS OF THE COMPLEXES

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Req.(%)</th>
<th>Found (%)</th>
<th>B(M)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M</td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>[Cu(A)]_2</td>
<td>3H_2O</td>
<td>24.96</td>
<td>37.71</td>
</tr>
<tr>
<td>[Ni(A)]_2</td>
<td>1.5H_2O</td>
<td>23.51</td>
<td>38.44</td>
</tr>
<tr>
<td>[Co(A)]_2</td>
<td>2H_2O</td>
<td>22.46</td>
<td>37.07</td>
</tr>
<tr>
<td>[Cu(en)]_2</td>
<td></td>
<td>18.28</td>
<td>41.43</td>
</tr>
<tr>
<td>[Ni(en)]_2</td>
<td></td>
<td>14.38</td>
<td>41.70</td>
</tr>
<tr>
<td>[Co(en)]_2</td>
<td></td>
<td>14.62</td>
<td>41.69</td>
</tr>
<tr>
<td>[Ni(en)]_2</td>
<td></td>
<td>17.28</td>
<td>26.11</td>
</tr>
<tr>
<td>[Ni(en)]_2</td>
<td></td>
<td>19.00</td>
<td>31.09</td>
</tr>
<tr>
<td>[Cu(en)]_2</td>
<td></td>
<td>16.74</td>
<td>37.94</td>
</tr>
<tr>
<td>[Ni(en)]_2</td>
<td></td>
<td>13.50</td>
<td>38.64</td>
</tr>
</tbody>
</table>

en = C_2H_4N_2; (A) = C_8H_8O_6 (terphthalate); and (B) = C_8H_4O_4S_4 (dithioterphthalate)