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Diffusion Coefficients in Aqueous Solutions of Beryllium Sulfate at 298 K

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Differential diffusion coefficients of beryllium sulfate in water at 298 K and at different concentrations have been measured using a conductimetric cell. The results are discussed on the basis of the Onsager–Fuoss theory. The results were interpreted with success, using the developments introduced by Pikal in the above theory. The cell uses an open-ended capillary method, and a conductimetric technique is used to follow the diffusion process by measuring the resistance of a solution inside the capillaries at recorded times.

Introduction

No data for the diffusion coefficients of beryllium sulfate solutions are reported in the *Handbook of Electrolyte Solutions* (*1*) nor, to our knowledge, anywhere else in the literature. There are also no data for the diffusion coefficients of electrolytes where Be^{2+} is the cation.

Our previous determinations of mutual diffusion coefficients for salts with ions that tend to form a number of complex species in aqueous solutions show considerable deviations from the Onsager–Fuoss treatment (*2*), as indeed the present one also shows, but the interest of this electrolyte is that it, being polyvalent but symmetrical, represents a good test for Pikal's theory (*3*).

Experimental Procedure

The apparatus which uses an open-ended capillary cell is essentially the same as that described elsewhere (*4*). The cell has two vertical capillaries, each closed at one end by a platinum electrode and positioned one above the other with the open ends separated by a distance of about 10 mm. The length of the capillaries is 24.70 mm.

The upper and lower tubes, initially filled with solutions of concentrations 0.75*c* and 1.25*c*, respectively, are surrounded with a solution of concentration *c*. This ambient solution is contained in a glass tank 200 × 140 × 60 mm immersed in a thermostat at 298.15 K. The tank is divided internally by Perspex sheets, and a glass stirrer creates a slow lateral flow of ambient solution across the open ends of the capillaries. The flow has been adjusted so that the concentration at each of the open ends is equal to the ambient solution value *c*. The stirrer is driven by a synchronous motor fed by a frequency generator and amplified to 220 V, the frequency being adjusted to the desired speed of the stirrer. Diffusion is followed by measuring the ratio of the resistances of the upper and lower tubes by an alternating current transformer bridge.

Experiments performed with 0.1 $mol{\cdot}dm^{-3}$ KCl solutions at different speeds show (*4*) that with a speed of 72 rpm the results coincide, within the experimental error, with those of Harned (*5*). The dependence of the measured diffusion coefficient *D* on the degree of stirring around the indicated speed on the stirrer (72 rpm) is negligible. This shows that the physical length of the capillary tube coincides with the diffusion path or, in other words, the boundary conditions described in ref 4 to solve Fick's second law of diffusion are applicable. Therefore, the so-called Δl effect (*6*) is reduced to negligible proportions. In fact, another apparatus built by V.M.L. at the Australian National University, Canberra, similar to the present one or that built at Cambridge, U.K., reproduced diffusion measurements in KCl solutions with good precision.

Table 1. Diffusion Experiments with 0.5 $mol{\cdot}dm^{-3}$ $BeSO_4$ Solutions at 298.15 K

$D_{obs}/(10^{-9}\ m^2{\cdot}s^{-1})$	TRa_∞[a]
0.6561	5082.8
0.6787	5082.5
0.6683	5082.5
0.6974	5082.0
$\bar{D} = 0.675$	$\sigma_D = 0.017$ (2.5%)

[a] $TRa_\infty = 10^4/(1 + w)$ where $w = R'/R''$ is the resistance ratio of the diffusion capillaries at infinite time. The close agreement of these readings indicates good reproducibility of the experimental conditions.

In order to measure the differential diffusion coefficient *D* at a given concentration *c*, a "top" solution of concentration 0.75*c* and a "bottom" solution of concentration 1.25*c* are prepared, each in a 2 L volumetric flask. The "bulk" solution of concentration *c* is prepared by mixing 1 L of the top solution with 1 L of the bottom solution, accurately measured. Beryllium sulfate solutions from 0.005 to 0.5 $mol{\cdot}dm^{-3}$ prepared from pro analysi BDH "Analar" reagent were studied. The cell and the whole apparatus were once more tested with potassium chloride solutions prepared from pro analysi grade KCl and dried as recommended by Duval (*7*), and the results are similar to those quoted in ref 8. The glass tank and the two capillaries are filled with a *c* solution, immersed in the thermostat, and allowed to come to thermal equilibrium. $TR_\infty = 10^4/(1 + w)$, where $w = R'/R''$ is the resistance ratio of the diffusion capillaries at infinite time (when their solutions are of concentration *c*), is now measured very accurately. The capillaries are then filled with the top and bottom solutions and allowed to diffuse into the bulk solution. Resistance ratio readings are taken at recorded times in intervals of about 5 min, for 1000 min after the beginning of the experiment. The diffusion coefficient is finally evaluated using a computerized linear least-squares procedure to fit the data. The theory developed for this cell has already been described (*4*).

Results and Discussion

The results of diffusion experiments in solutions of 0.5 $mol{\cdot}dm^{-3}$ $BeSO_4$ at 298.15 K are shown in Table 1. They

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Table 2. Diffusion Coefficients of $BeSO_4$ Solutions at 298.15 K

c/(mol·dm^{-3})	D/(10^{-9} m^2·s^{-1})[a]	TRa_∞[b]	σ_D[c]
50×10^{-2}	0.668	5082.4	0.011
30×10^{-2}	0.718	5041.2	0.014
20×10^{-2}	0.742	4999.0	0.001
10×10^{-2}	0.778	4993.1	0.023
8×10^{-2}	0.736	4988.5	0.012
5×10^{-2}	0.816	4970.3	0.008
3×10^{-2}	0.805	4952.3	0.024
1×10^{-2}	1.043	4917.4	0.024
8×10^{-3}	0.936	5065.9	0.078
5×10^{-3}	1.309	5087.7	0.015

[a] Mean value of D in three experiments. [b] Mean value of TRa_∞ as defined in Table 1. [c] Standard deviation for three experiments.

Table 3. Diffusion Coefficients of 0.1 mol·dm^{-3} KCl Solutions at 298.15 K

D_{obs}/(10^{-9} m^2·s^{-1})	TRa_∞[a]
1.865	4993.2
1.863	4995.0
1.848	4995.1
1.886	4995.9
$\bar{D} = 1.865$	$\sigma_D = 0.016$ (0.85%)

[a] Mean value of TRa_∞ as defined in Table 1.

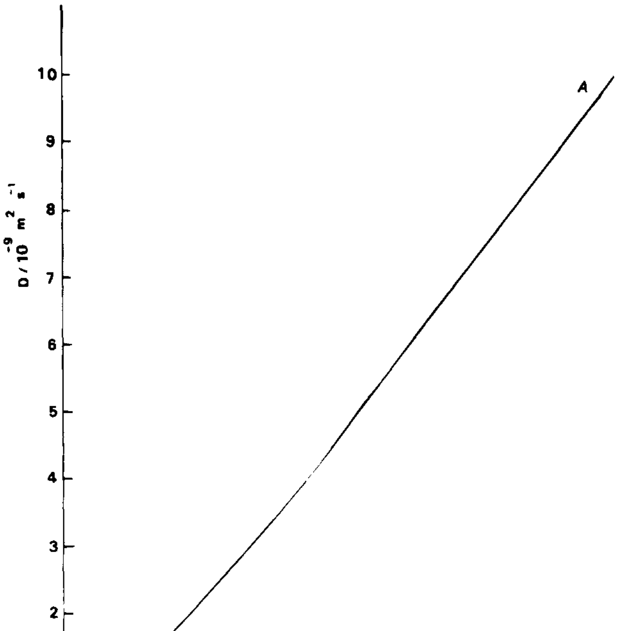

Figure 1. Comparison of diffusion coefficients for $BeSO_4$–H_2O with Onsager–Fuoss and Pikal theories (curves A and B), using the value of the ion size parameter by Kielland ($a = 6 \times 10^{-10}$ m) and our results (●).

indicate the precision of the method for measuring differential diffusion coefficients. Measurements in 0.1 mol·dm^{-3} KCl solutions by this method (Table 3) agree with those of Harned (*5*) within 1%. Table 2 shows the results with beryllium sulfate solutions from 5×10^{-3} to 5×10^{-1} mol·dm^{-3} at 298.15 K. Results are the average of three or four experiments performed on consecutive days. In Figures 1 and 2 our data are compared with the Onsager–Fuoss (*2*) theory and with the equation revised by Pikal (*3*).

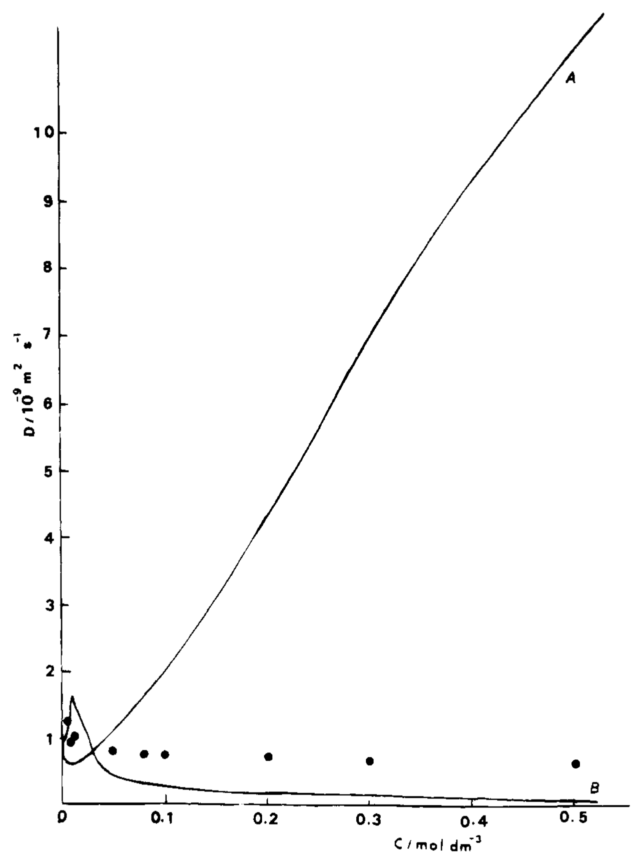

Figure 2. Comparison of diffusion coefficients for $BeSO_4$–H_2O with Onsager–Fuoss and Pikal theories (curves A and B), using the value of the ion size parameter by the best fit of the curve activity coefficient vs concentration ($a = 3 \times 10^{-10}$ m) and our results (●).

Figure 1 also shows the curve resulting from the application of the Onsager–Fuoss theory to from 0.0 to 0.5 mol·dm^{-3} $BeSO_4$ solutions. It is clearly seen that the results deviate significantly from our results. This is not surprising if we take into account the formation of complexes between Be^{2+} and SO_4^{2-} of the type $Be(SO_4)_x^{2-2x}$ and the variety of ion pairs eventually formed, factors not taken into account in the formation of the Onsager–Fuoss equation (*2*). Formation of ion pairs can be accounted for in the Onsager–Fuoss treatment (*9*), resulting in the expression

$$D_{ip}/D_{OF} = 1 + (1 - \alpha)\left[\lambda_m^\circ\left(\frac{1}{\lambda_1^\circ} + \frac{1}{\lambda_2^\circ}\right) - 1\right] \qquad (1)$$

where a correction factor between the diffusion coefficient taking into account the ion pair formation and that calculated from the Onsager–Fuoss theory, D_{ip}/D_{OF}, is given as a function of the degree of dissociation α and of the equivalent conductances of the ions involved and the ion pair, λ_1°, λ_2°, and λ_m°. However, this does not clarify matters because we do not have data for the parameters involved.

Assuming eq 1 is valid in the present case, we may attempt estimations of α and λ_m° from the measured D values of Table 2 taken as D_{ip}. $\lambda^\circ(SO_4^{2-})$ is given in the literature as 79.8 S·cm^2 (*10*). $\lambda^\circ(Be^{2+})$ is cited in ref 10 as 45.0 S·cm^2. The Onsager–Fuoss values D_{OF} were calculated using the values of $\phi(\kappa a)$ vs concentration indicated by Harned and Owen (*11*) (adjusted by a least-squares procedure to an appropriate curve) and taking R, 0, and ϵ from ref 12 and other reliable sources.

It seems appropriate to estimate $\lambda_m°$ from the D values at lowest concentration, 0.005 mol·dm^{-3}, and then use it to estimate α at other concentrations. Thus, taking $\alpha = 0.70$ in the case of a 0.005 mol·dm^{-3} (*9, 13*) $BeSO_4$ solution, we have from eq 1), $\lambda_m° = 153.5$ S·cm^2.

Then, also from eq 1, calculations led to $\alpha = 0.87$ for 0.008 mol·dm^{-3}, $\alpha = 0.83$ for 0.01 mol·dm^{-3}, $\alpha = 0.96$ for 0.03 mol·dm^{-3}, $\alpha = 0.98$ for 0.05 mol·dm^{-3}, $\alpha = 1.08$ for 0.08 mol·dm^{-3}, $\alpha = 1.10$ for 0.1 mol·dm^{-3}, $\alpha = 1.15$ for 0.2 mol·dm^{-3}, $\alpha = 1.16$ for 0.3 mol·dm^{-3}, and $\alpha = 1.17$ for 0.5 mol·dm^{-3} $BeSO_4$ solution. It is obvious from these values (showing α increasing with the concentration) that the method is inapplicable to the present electrolyte.

On the other hand, Pikal (*3*) has developed a theory of mutual diffusion in a binary electrolyte "using the conventional charged sphere-in-continuum model. However, instead of approximating the Boltzman exponential by a truncated power series, the calculations are performed retaining the full Boltzman exponential. As a result of this procedure, a term representing the effect of ion-pair formation appears in the theory as a natural consequence of the electrostatic interactions. The mobility of an ion pair is not an adjustable parameter, but it is determined by the theory."

In fact, from Figures 1 and 2, we see that the Pikal curve is more applicable to the experimental curve than the Onsager–Fuoss curve.

The theoretical curves were carried out using the values of the ion size parameter "*a*" calculated by Kielland (*14*) and by the best fit of the curve activity coefficient vs concentration, obtained by the Debye–Huckel equation (*15*).

In conclusion, we suggest the use of Pikal's equation on other systems of the same type, when no experimental values are available.

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