



Diffusion Coefficients in Aqueous Solutions of Potassium Chloride at High and Low Concentrations

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Differential diffusion coefficients of potassium chloride in water at 298.15 K, and at concentrations from 0.001 M to 1 M, have been measured using a conductimetric cell and an automatic apparatus to follow diffusion. The results are discussed on the basis of the Robinson and Stokes, Onsager–Fuoss and Pikal models. 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.

1. Introduction

Mutual differential isothermal diffusion coefficients of electrolytes in aqueous solutions have been measured in our laboratory using an open-ended capillary cell [1–12], Fig 1, developed some years ago. Diffusion may be followed by measuring the ratio of electrical resistances of the electrolyte solution in both capillaries as time proceeds, using an alternating current transformer bridge and an oscilloscope where an ellipse is manually reduced to an horizontal line. Attempts to use an automatic system to continuously measure the resistance ratios have, until now, been successful only for capillary resistances of the order of 5 k Ω , or lower, that is, electrolyte concentrations of the order of 0.1 M or higher. In fact, whereas with the manual system it is possible to measure the pure ohmic resistance, by manually balancing the capacity effects, and therefore go to concentration of 0.001 M, the automatic system measures impedance ratios.

The present paper reports the experimental alterations which enabled us to successfully use the automatic system, in conditions of very high electrical resistance of the solutions inside the capillaries (which will facilitate research on this field), presents data obtained at high and low KCl concentrations, and discusses them on the basis of the Robinson and Stokes [13], Onsager–Fuoss [14] and Pikal [15] models.

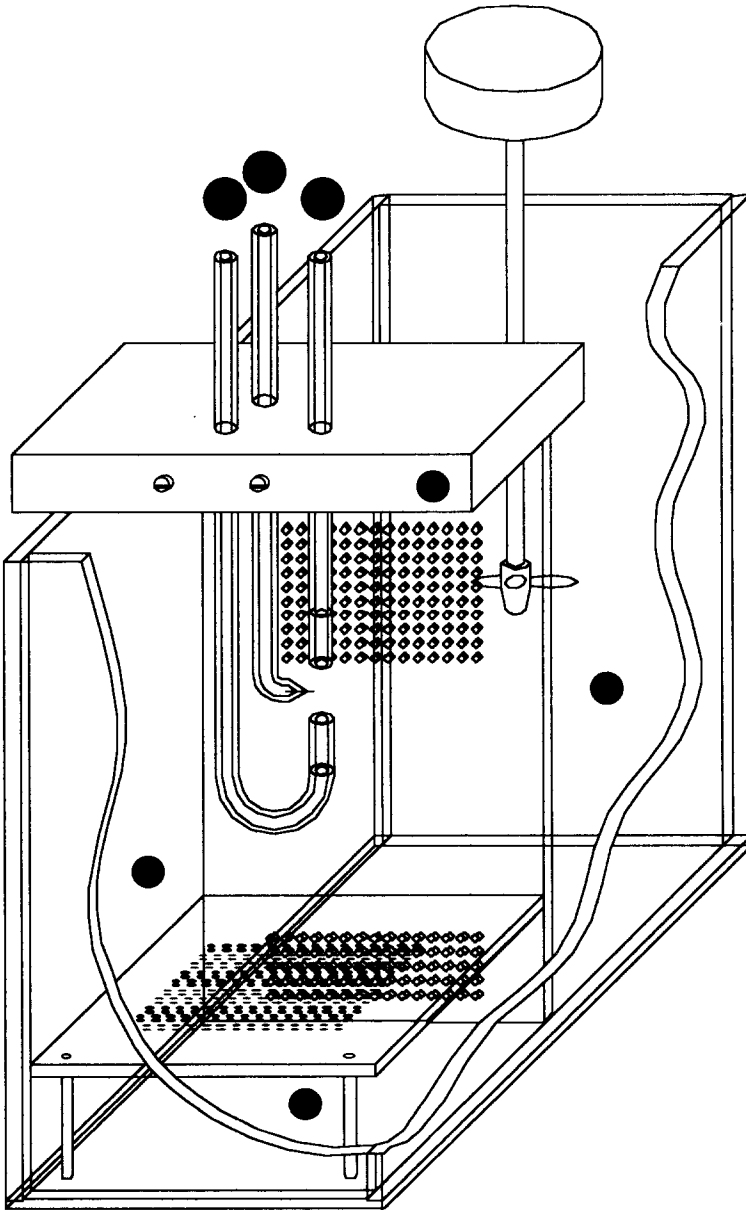


Figure 1 — Diffusion cell developed by Lobo

The apparatus assembled for use with the open-ended capillary cell in this laboratory, Fig. 1, is essentially the same as previously reported [2]. 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 upper and lower tubes, initially filled with solutions of concentrations $0.75c$ and $1.25c$, respectively, are surrounded with a solution of concentration c . This ambient solution is contained in a glass tank $200 \times 140 \times 60$ 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. Experimental conditions are such that the concentration at each of the open ends is equal to the ambient solution value c , that is the physical length of the capillary tube coincides with the diffusion path or, in other words, the boundary conditions described in [2] to solve Fick's second law of diffusion are applicable. Therefore, the so-called Δl -effect [2] is reduced to negligible proportions. In a manual apparatus, diffusion is followed by measuring the ratio of resistances of upper and lower tubes by an alternating current transformer bridge. In an automatic apparatus $w = R_t/R_b$ is measured by a Solartron digital voltmeter (DVM) 7061 with $6\frac{1}{2}$ digits. A power source Bradley Electronics Model 232 supplies a 30 V sinusoidal signal of 4 kHz (stable up to 0.1 mV) to a potential divider that applies a 250 mV signal to the platinum electrodes at the top and bottom capillaries. By measuring the voltages V' and V'' from the top and bottom electrodes to the central electrode at ground potential, in a fraction of a second, the DVM calculates $w = R_t/R_b$.

In order to measure the differential diffusion coefficient D at a given concentration c , a "top" solution of concentration $0.75c$ and a "bottom" solution $1.25c$ are prepared, each in a 2 litre volumetric flask. The "bulk" solution of concentration c is prepared by mixing 1 litre of "top" solution with 1 litre of "bottom" solution, accurately measured. The potassium chloride solutions were prepared from *pro analysi* grade Fluke reagent, dried at 393 K, and the results are similar to those quoted in [5]. The glass tank and the two capillaries are filled with c solution, immersed in the thermostat, and allowed to come to thermal equilibrium. $TR_\infty = 10^4/(1 + w_\infty)$, where $w_\infty = R_t/R_b$ is the resistance ratio of the top (t) and bottom (b) diffusion capillaries at infinite time (when their solutions are c), is now measured very accurately. $TR = 10^4/(1 + w)$, where $w = R_t/R_b$ is the equivalent, at any time t .

The capillaries are then filled with "top" and "bottom" solutions and allowed to diffuse into the "bulk" solution. Resistance ratio readings are taken at recorded times, beginning $1\ 000$ min after starting the experiment. The diffusion coefficient is finally evaluated using a linear least-squares procedure to fit the data and subsequently an iterative process by using 20 terms of the expansion series of the solution of Ficks 2nd

law for the present boundary conditions. The theory developed for this cell has already been described [2].

3. Results and discussion

Data on diffusion coefficients previously reported [1-12] were measured using a manual system where resistance ratios $w = R_t/R_b$ were manually taken every five minutes for a period of about 8 hours with an applied signal of 4 000 Hz. An automatic system was used only for concentrations down to around 0.1 M where the resistance inside the capillaries is of the order of a few thousands of ohms. For lower concentrations, that is, for resistances of the order of tens of thousands or hundreds of thousands of ohms (solutions of the order of 0.01 M or 0.001 M), the automatic system did not give reliable values, as shown in simulations similar to those indicated in Table 1.

In the present work we overcame this difficulty by using frequencies lower than the 4 000 Hz previously taken as the most appropriate. Experimentation showed no problems of electrode polarization.

Simulations of actual experiments for measuring diffusion coefficients in 1.0 M, 0.1 M, 0.01 M and 0.001 M KCl solutions using resistors set up so as to simulate the critical phases of those experiments with the present cell, showed that this procedure is reliable. Such was confirmed by measurements with those solutions. For the present purpose, the conclusions taken using KCl as the electrolyte are applicable to most other electrolytes, for obvious reasons.

Table 1 shows the results obtained by simulating electrolyte solutions of different concentration inside the capillaries of the open ended capillary cell with variable resistors. Frequencies from 30 to 10 000 Hz have been used. When the actual cell is filled with 1.0 M, 0.1 M and 0.01 M KCl solutions the actual resistance is approximately $R_t = R_b = 500.0 \Omega$, $R_t = R_b = 5\,000.0 \Omega$ and $R_t = R_b = 50\,000 \Omega$, respectively, where R_t and R_b are the resistances of the top and bottom capillaries, respectively. Therefore, in the present simulations we used resistors with these values of R_t and R_b in both "capillaries" to simulate infinite conditions.

To simulate the starting procedure where the top and bottom capillaries are filled with solutions 0.75 c and 1.25 c, where c is the bulk solution (1.0 M, 0.1 M, 0.01 M), the following values were used in the resistors: $R_t = 600.0 \Omega$ and $R_b = 400.0 \Omega$; $R_t = 6\,000.0 \Omega$ and $R_b = 4\,000.0 \Omega$; $R_t = 60\,000 \Omega$ and $R_b = 40\,000 \Omega$.

To simulate the end of an experiment, at approximately 1 440 minutes, the following values were used in the resistors: $R_t = 550.0 \Omega$ and $R_b = 450.0 \Omega$; $R_t = 5\,500.0 \Omega$ and $R_b = 4\,500.0 \Omega$; $R_t = 55\,000 \Omega$ and $R_b = 45\,000 \Omega$.

TR_{ideal} in Table 1 represents the value TR (as previously defined) which should be observed with those resistors. TR_{auto} is the value actually measured using a signal of the indicated frequency.

Table 1
Values of $\Delta TR = TR_{\text{auto}} - TR_{\text{ideal}}$ with different "top" and "bottom" resistors, R_t and R_b , and with varying applied signal frequencies

Experiment simulated	R_t/Ω	R_b/Ω	TR_{ideal}	TR_{auto}	f/Hz	ΔTR a)
Capillaries with solution c = 1 M (t = ∞)	500	500	5 000.0	4 984.5	30	-15.7
				4 979.0	60	-21.0
				4 978.9	120	-21.1
				4 978.5	250	-21.5
				4 979.0	480	-21.0
				4 979.1	1 000	-20.9
				4 978.3	2 000	-21.7
				4 977.7	3 000	-22.3
				4 978.2	4 000	-21.8
				4 978.3	5 000	-21.7
				4 977.0	6 000	-23.0
				4 977.2	7 000	-22.8
				4 977.0	8 000	-23.0
				4 979.2	9 000	-20.8
4 979.3	10 000	-20.7				
Start of an experiment (t = 0 s)	600	400	4 000.0	4 054.1	30	+54.1
				3 984.5	60	-15.5
				3 985.8	120	-14.2
				3 985.8	250	-14.2
				3 985.7	480	-14.3
				3 986.1	1 000	-13.9
				3 986.3	2 000	-13.7
				3 985.6	3 000	-14.4
				3 985.8	4 000	-14.2
				3 986.6	5 000	-13.4
				3 992.5	6 000	-7.5
				3 984.0	7 000	-16.0
				3 982.5	8 000	-17.5
				3 988.0	9 000	-12.0
3 988.2	10 000	-11.8				
End of an experiment (t > 86 400 s)	550	450	4 500.0	4 491.0	30	-9.0
				4 481.0	60	-19.0
				4 481.5	120	-18.5
				4 481.9	250	-18.1
				4 482.0	480	-18.0
				4 482.1	1 000	-17.9
				4 482.1	2 000	-17.9
				4 481.3	3 000	-18.7
				4 481.9	4 000	-18.1
				4 482.2	5 000	-17.8
				4 485.5	6 000	-14.5
				4 485.9	7 000	-14.1
				4 479.5	8 000	-20.5
				4 429.1	9 000	-70.9
4 484.1	10 000	-15.9				

Note: a) Low $|\Delta TR|$ values indicate appropriate signal frequencies for the use of the present cell (Fig. 1).

Table 1
(Cont.)

Experiment simulated	R_t/Ω	R_b/Ω	TR_{ideal}	TR_{auto}	f/Hz	ΔTR a)
Capillaries with solution $c = 0.1$ M ($t = \infty$)	5 000	5 000	5 000.0	4 977.5	30	-22.5
				4 980.0	60	-20.0
				4 980.1	120	-19.9
				4 980.3	250	-19.7
				4 980.2	480	-19.8
				4 980.8	1 000	-19.2
				4 981.7	2 000	-18.3
				4 984.0	3 000	-16.0
				4 985.6	4 000	-14.4
				4 987.8	5 000	-12.2
				4 979.3	6 000	-20.7
				4 979.0	7 000	-20.7
				4 978.0	8 000	-22.0
				4 999.6	9 000	-0.4
5 002.9	10 000	+2.9				
Start of an experiment ($t = 0$ s)	6 000	4 000	4 000.0	3 995.0	30	-5.0
				3 996.1	60	-3.9
				3 995.4	120	-4.6
				3 995.8	250	-4.2
				3 996.5	480	-3.5
				3 998.7	1 000	-1.3
				4 004.6	2 000	+4.6
				4 014.0	3 000	+14.0
				4 025.4	4 000	+25.4
				4 037.8	5 000	+37.8
				3 995.0	6 000	-5.0
				3 995.0	7 000	- 5.0
				3 995.1	8 000	-4.9
				4 115.3	9 000	+115.3
4 136.3	10 000	+136.3				
End of an experiment ($t > 86\,400$ s)	5 500	4 500	4 500.0	4 480.9	30	-19.1
				4 487.5	60	-12.5
				4 487.2	120	-12.8
				4 487.5	250	-12.5
				4 487.9	480	-12.1
				4 489.4	1 000	-10.6
				4 492.9	2 000	-7.1
				4 499.0	3 000	-1.0
				4 505.5	4 000	+5.0
				4 512.8	5 000	+12.8
				4 486.5	6 000	-13.5
				4 486.9	7 000	-13.1
				4 487.1	8 000	-12.9
				4 558.9	9 000	+58.9
4 571.2	10 000	+71.2				

Note: a) Low ΔTR values indicate appropriate signal frequencies for the use of the present cell (Fig. 1).

Table 1
(Cont.)

Experiment simulated	R_T/Ω	R_P/Ω	TR_{ideal}	TR_{auto}	f/Hz	ΔTR a)
Capillaries with solution c = 0.01 M (t = ∞)	50 000	50 000	5 000.0	4 979.6	30	-20.4
				4 984.8	60	-15.2
				4 985.3	120	-14.7
				4 986.8	250	-13.2
				4 991.1	480	-8.9
				5 006.2	1 000	+6.2
				5 042.8	2 000	+42.8
				5 078.5	3 000	+78.5
				5 101.6	4 000	+101.6
				5 113.8	5 000	+113.8
				4 984.3	6 000	-15.7
				4 984.4	7 000	-15.6
				4 985.0	8 000	-15.0
				5 136.0	9 000	+136.0
5 141.8	10 000	+141.8				
Start of an experiment (t = 0 s)	60 000	40 000	4 000.0	3 995.0	30	-5.0
				4 111.4	60	+111.4
				4 114.3	120	+114.3
				4 121.8	250	+121.8
				4 143.5	480	+143.5
				4 223.6	1 000	+223.6
				4 418.0	2 000	+418.0
				4 614.7	3 000	+614.7
				4 752.4	4 000	+752.4
				4 853.6	5 000	+853.6
				4 093.5	6 000	+ 93.5
				4 099.3	7 000	+99.3
				4 102.1	8 000	+102.1
				5 031.0	9 000	+1031.0
5 051.3	10 000	+1051.3				
End of an experiment (t > 86 400 s)	55 000	45 000	4 500.0	4 486.8	30	-13.2
				4 549.7	60	+49.7
				4 551.6	120	+51.6
				4 555.6	250	+55.6
				4 569.0	480	+69.0
				4 617.9	1 000	+117.9
				4 735.1	2 000	+235.1
				4 852.5	3 000	+352.5
				4 932.9	4 000	+432.9
				4 989.2	5 000	+489.2
				4 549.5	6 000	+49.5
				4 535.5	7 000	+35.5
				4 539.3	8 000	+39.3
				5 086.7	9 000	+586.7
5 099.4	10 000	+599.4				

Note: a) Low ΔTRI values indicate appropriate signal frequencies for the use of the present cell (Fig.1).

$\Delta Tr = (TR_{\text{auto}} - TR_{\text{ideal}})$ shows that for lower values of R_t and R_b any frequency from 30 to 10 000 Hz could be used; for higher values of R_t and R_b high frequencies give large deviations, but low frequencies give deviations which do not introduce significant errors in measuring diffusion coefficients in a similar way according to the symmetry of the measuring cell and to the fact that we are interested in the rate of variation of the resistance ratio $w = R_t/R_b$, and not in the absolute values of such ratio.

Table 2 shows good reproducibility in the results for 4 consecutive KCl 0.1 M diffusion experiments using a 4 000 Hz signal.

Table 2
Diffusion experiments with 0.1 M KCl aqueous solutions at 298.15 K and frequency 4 000 Hz

$D/$ $/10^{-9} \text{ m}^2 \text{ s}^{-1}$	TR_{∞}
1.863	4 995.0
1.848	4 995.1
1.821	4 995.0
1.865	4 994.9

($\bar{D} = 1.849 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$; $S_{\bar{D}} = 0.010 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$)

Table 3
Diffusion coefficients D of KCl aqueous solutions at 298.15 K at different concentrations c and appropriate frequencies.

c $/\text{mol dm}^{-3}$	Frequency/ $/\text{Hz}$	Mean value of D in 4 experiments/ $/10^{-9} \text{ m}^2 \text{ s}^{-1}$	$S_{\bar{D}}/$ $/10^{-9} \text{ m}^2 \text{ s}^{-1}$ a)
1×10^{-3}	250	1.964	0.025
2×10^{-3}	250	1.983	0.045
3×10^{-3}	500	1.985	0.014
5×10^{-3}	500	1.963	0.020
8×10^{-3}	500	1.945	0.025
1×10^{-2}	4 000	1.891	0.001
5×10^{-2}	4 000	1.893	0.007
1×10^{-1}	4 000	1.849	0.010
2×10^{-1}	4 000	1.830	0.010
5×10^{-1}	4000	1.867	0.002
10×10^{-1}	4 000	1.891	0.012

a) $S_{\bar{D}}$ is the standard deviation of the mean of 4 experiments.

Table 3 summarizes the average of 4 diffusion experiments at each KCl concentration value from 10^{-3} M to 1 M. Reproducibility of the results is good, as shown by S_D , and its mean is in good agreement with our previous results with the manual system, and with Miller's [16] and Harned's [17], as shown in Fig. 2. Table 3 shows that the most appropriate measuring frequency increases with concentration.

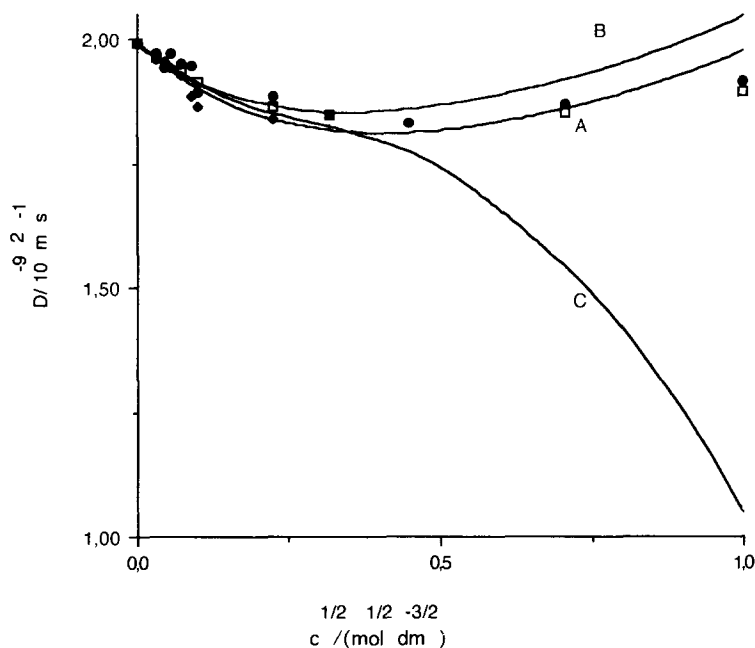


Figure 2 — Comparison of diffusion coefficients for KCl—H₂O with Robinson-Stokes, Onsager-Fuoss and Pikal models (curves A, B and C), using the value of ion size parameter by Kielland ($a = 3.5 \times 10^{-10}$ m) and our results (•), at the temperature of 298.15 K. Other experimental results by Miller (□) and Harned (◆).

Fig. 2 compares experimental results with curves drawn on the basis of Robinson and Stokes [13], Onsager and Fuoss [14] and Pikal [15] models. For dilute solutions the experimental data and all three models are in reasonable agreement; for higher concentrations, the experimental data from ourselves and other researchers are in good agreement but the curves from the above models differ considerably from experimental observation. This is to be expected from the limitations of the above models.

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