

THE OPEN-ENDED CAPILLARY CELL - A METHOD TO MEASURE A LARGE RANGE OF CONCENTRATIONS OF ELECTROLYTE AQUEOUS SOLUTIONS

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The open-ended capillary cell has been used as a reliable method to measure mutual differential diffusion coefficients of a great variety of aqueous solutions of electrolytes [1, 2]. In the last few years we have been developing, with some success, a capillary cell capable of measuring thermodynamic diffusion coefficients of electrolytes imbibed in polymeric matrices [3-5]. We have developed two different systems, called "manual" and "automatic", to measure diffusion coefficients.

In this communication we will present an improvement of the "manual" system that permit us to measure a large range of concentrations, from approximately 10^{-3} M until at least 2 M, with very good precision, and accuracy.

In fact the open-ended capillary system is based in measurements with a RLC system as we can see in a schematic diagram presented in figure 1.

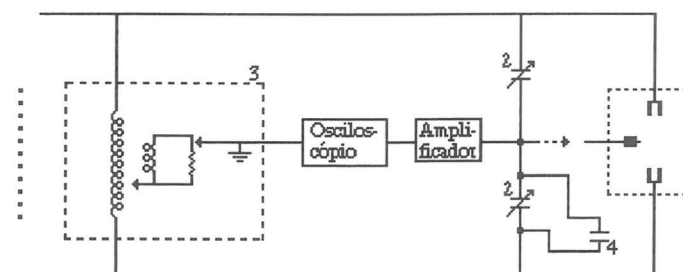


Figure 1 - Schematic diagram of the whole system of the open-ended capillary cell. 1) Diffusion cell; 2) Variable capacity box; 3) Ratio transformer; 4) Capacitors.

In Fig. 1 we see that the signal coming from the diffusion cell (see 1 in Fig. 1) has three components. The capacitive component is nulled with a variable capacity box (2 in Fig. 1), and it is possible to prove that R'/R'' is equal to L/L'' , which is measured with a ratio transformer (3 in Fig. 1). The improvement consists basically in increasing the capacitance (4 in the Fig. 1) of the one of the variable capacity boxes, adding capacitor according to the concentration of the electrolyte solutions (Table 2).

Table 2 - Effect of the concentration of the KCl solution on the capacitance of the electric system

[KCl] / M	Capacitance / pF
≤ 0.1	1100 (variable capacity)
$0.2 \leq [\text{KCl}] \leq 0.4$	2200
$0.5 \leq [\text{KCl}] \leq 1.0$	4400
2.0	5900

Table 3 presents the differential diffusion coefficients of KCl solutions. These results show a very good precision as well as the good agreement with the results obtained by other experimentalists [6, 7].

The diffusion coefficients obtained were also compared (Figure 1) with diffusion coefficients (D_A) computed from Agar's [8] equation:

$$D_A = D_{OF} \left(1 - 0.018 n m \right) \left[1 + 0.018 m \left(v \frac{D_{H_2O}^*}{D^0} - n \right) \right] \frac{\eta_0}{\eta} \quad (1)$$

D_{OF} is the diffusion coefficient computed through Onsager-Fuoss equation (diffusion coefficient corrected for the electrophoretic effect, m is the molality of the electrolyte solution, n is the hydration number, $D_{H_2O}^*$ is the selfdiffusion coefficient of water, D^0 is the

Nernst limiting diffusion coefficient, η_0/η is the relative viscosity of the solution and v is the number of ions formed from one molecule of solute.

Table 3 - Mutual Differential Diffusion Coefficients of KCl solutions, at 298 K.

	[KCl] / M	TR ∞	n° of experimental data	$\Delta t/\text{min}$	Random Error/%	$D/10^{-5} \text{ cm}^2 \text{ s}^{-1}$	$D_{\text{obs}} (\pm \sigma) / 10^{-5} \text{ cm}^2 \text{ s}^{-1}$
1.2	0,1	4882,1	47	422,8	6,29E-2	1,771	1,867 ($\pm 1,240\text{E-1}$)
1.3		4880,0	49	376,3	8,27E-2	1,860	
1.1.A		5059,3	50	349,4	3,401E-2	1,946	
1.2.A		5040,7	50	305	4,636E-2	1,674	
1.3.A		5040,5	50	311,5	1,740E-2	1,985	
1.4.A		5038,8	50	207	4,105E-2	1,968	
2.1	0,2	5052,5	51	394,9	3,097E-2	1,807	1,845 ($\pm 9,734\text{E-2}$)
2.2		5083,2	54	379,7	3,117E-2	1,773	
2.3		5083,2	52	383	4,537E-2	1,956	
3.1	0,3	5107,6	50	320	1,168E-2	1,842	1,832 ($\pm 2,145\text{E-2}$)
3.2		5120,7	50	295	5,827E-2	1,807	
3.3		5117,6	50	377	2,318E-2	1,846	
4.2	0,4	5153,8	50	420,5	5,203E-2	1,863	1,827 ($\pm 3,126\text{E-2}$)
4.4		5161,4	50	378,5	1,956E-2	1,805	
4.5		5162,1	50	358,7	3,504E-2	1,813	
5.3	0,5	5169,0	50	397,7	3,411E-2	1,825	1,816 ($\pm 1,965\text{E-2}$)
5.6		5169,3	50	353	1,328E-2	1,820	
5.7		5167,2	50	380,3	3,949E-2	1,830	
5.8		5165,7	50	401,4	4,405E-2	1,787	
6.2	0,6	5195,3	50	390	5,953E-2	1,823	1,840 ($\pm 3,150\text{E-2}$)
6.3		5187,1	50	415	3,643E-2	1,876	
6.4		5194,4	53	360	5,741E-2	1,820	
7.1	0,7	5088,1	56	400,7	3,360E-2	1,934	1,886 ($\pm 4,457\text{E-2}$)
7.2		5085,1	55	410	2,156E-2	1,845	
7.3		5097,2	57	403	2,461E-2	1,879	
10.1	1,0	5032,6	52	380	0,2416	1,938	1,936 ($\pm 5,363\text{E-3}$)
10.2		5028,6	55	353	0,1092	1,930	
10.3		5029,4	54	374,1	0,1178	1,941	
20.1	2,0	5068,8	51	400	0,1094	2,071	2,049 ($\pm 2,430\text{E-2}$)
20.2		5076,9	54	403,9	0,1040	2,023	
20.3		5086,6	56	405	0,1669	2,052	

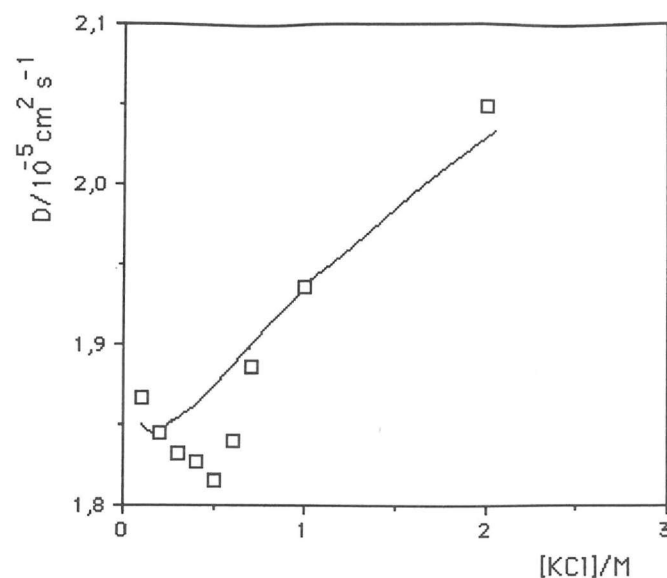


Figure 3 - Comparison of experimental diffusion coefficients (□), of concentrated KCl solutions, with those calculated from Agar's equation (—).

From figure 1 we can see that there is a suitable agreement between the experimental and a theoretical diffusion coefficients to concentrations higher than 0.5 M.

For all these reasons the open-ended capillary cell shows once more its great application to the study of the electrolyte solutions in a large range of concentrations, with good precision and accuracy.

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