Theoretical aspects 1.1. Concepts of diffusion Diffusion data of electrolytes in aqueous solutions are of great interest not only for fundamental purposes (providing a detailed comprehensive information - both kinetic and thermodynamic), but also for many technical fields such as corrosion studies [1-3]. The gradient of chemical potential in the solution is the force producing the irreversible process which we call diffusion [1-3]. However, in most solutions, that force may be attributed to the gradient of the concentration at constant temperature. Thus, the diffusion coefficient, D, in a binary system, may be defined in terms of the concentration gradient by a phenomenological relationship, known as Fick´s first law, (1.1) or, considering only one dimension for practical reasons, (1.2) where J represents the flow of matter across a suitable chosen reference plane per area unit and per time unit, in a one-dimensional system, and c is the concentration of solute in moles per volume unit at the point considered; (1.1) may be used to measure D. The diffusion coefficient may also measured considering Fick’s second law, in one dimensional system, (1.3) In general, the available methods are grouped into two groups: steady and unsteady-state methods, according to (1.2) and (1.3). Diffusion is a three-dimensional phenomenon, but many of the experimental methods used to analyze diffusion restrict it to a one dimensional process [1-4]. The resolution of equation (1.2) is much easier if we consider D as a constant. This approximation is applicable only when there are small differences of concentration, which is the case in our open-ended condutimetric technique [3,5], and in the Taylor technique [3,6,7]. In these conditions, it is legitimate to consider that our measurements of differential diffusion coefficients obtained by the above techniques are parameters with a well defined thermodynamic meaning [3-7]. 1.2 Effect of the hydrolysis on diffusion of electrolytes in aqueous solutions A theory of mutual diffusion of electrolytes in aqueous solutions capable of accurately predicting diffusion coefficients has not yet been successfully developed, due to the complex nature of these systems. However, Onsager and Fuoss equation (1.4) [8], has allowed the estimation of diffusion coefficients with a good approximation for dilute solutions and symmetrical electrolytes of the type 1:1. This equation may be expressed by (1.4) where D is the mutual diffusion coefficient of the electrolyte, the first term in parenthesis is the activity factor, is the mean molar activity coefficient, c is the concentration in mol dm^{-3}, is the Nernst limiting value of the diffusion coefficient (Eq. (1.4)), and Δn are the electrophoretic terms given by (1.5) where kB is the Boltzmann’s constant; T is the absolute temperature; An are functions of the dielectric constant, of the solvent viscosity, of the temperature, and of the dimensionless concentration-dependent quantity (ka), k being the reciprocal of average radius of the ionic atmosphere; and are the limiting transport numbers of the cation and anion, respectively. Since the expression for the electrophoretic effect has been derived on the basis of the expansion of the exponential Boltzmann function, because that function is consistent with the Poisson equation, we only would have to take into account the electrophoretic term of the first and the second order ($n = 1$ and $n = 2$).

Thus, the experimental data Dexp can be compared with the calculated DOF on the basis of Eq. (1.6) (1.6) It was observed and reported in the literature a good agreement between the observed values and those calculated by equation (1.6) for potassium chloride [9] and magnesium nitrate [10], but for cobalt chloride [11] and beryllium sulphate [12] they are definitely higher than theory predicts. This is not surprising, if we take into account the change with concentration of parameters, such as viscosity, hydration and hydrolysis, factors not taken into account in Onsager-Fuoss model [8]. In fact, those differences may possibly be due to hydrolysis of the cations (eq. 1.7) [13-15], which would be more pronounced in cobalt chloride and beryllium sulphate than potassium chloride and magnesium nitrate. (1.7) We are proposing a model in order to allow the estimation of the amount of ion H+(aq) produced in each of the systems studied, using experimental diffusion coefficients determined by our condutimetric method and the respective predictive by that theory. That is, having in mind the acidic character of some cations [14,15], the percentages ion H+(aq) produced (or the amount of acid that would be necessary to add a given electrolyte solution in the absence of hydrolysis in order to simulate a more real system) are determined by the following system (Eqs. 1.8 and 1.9), Dacid z + Delectrolyte y = Dexp (1.8) z + y = 1 (1.9) being z x 100 and y x 100 the percentages of acid and electrolyte, respectively, and Dexp, our values of the diffusion coefficients of electrolytes in aqueous solutions, and Dacid and Delectrolyte, the Onsager and Fuoss values of the diffusion coefficients for the acids and electrolytes, respectively, in aqueous solutions. 2. Experimental aspects Conductimetric technique An open-ended capillary cell (Fig. 1) [5], which has been used to obtain mutual diffusion coefficients for a wide variety of electrolytes [5,9-13,16-19], has been described in great detail [5]). Basically, it consists of 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 14 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 bath at 25 ºC. Perspex sheets divide the tank internally 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. This means that the required boundary conditions described in the literature [5] to solve Fick´s second law of diffusion are applicable. Therefore, the so-called Dl effect [5] is reduced to negligible proportions. In our manually operated apparatus, diffusion is followed by measuring the ratio w=Rt/Rb of resistances Rt and Rb of the upper and lower tubes by an alternating current transformer bridge. Fig. 1 - TS, BS: support capillaries; TC, BC: top and bottom diffusion capillaries; CE: central electrode; PT: platinum electrodes; D1, D2: perspex sheets; S: glass stirrer; P: perspex block; G1, G2: perforations in perspex sheets; A, B: sections of the tank; L1, L2: small diameter coaxial leads [5] In our automatic apparatus, w is measured by a Solartron digital voltmeter (DVM) 7061 with 6 1/2 digits. A power source (Bradley Electronic Model 232) supplies a 30 V sinusoidal signal at 4 kHz (stable to within 0.1 mV) to a potential divider that applies a 250 mV signal to the platinum electrodes in the top and bottom capillaries. By measuring the voltages V’ and V’’ from top and bottom electrodes to a central electrode at ground potential in a fraction of a second, the DVM calculates w. In order to measure the differential diffusion coefficient D at a given concentration c, the bulk solution of concentration c is prepared by mixing 1 L of “top” solution with 1 L of “bottom” solution, accurately measured. The glass tank and the two capillaries are filled with c solution, immersed in the thermostat, and allowed to come to thermal equilibrium. The resistance ratio w = w¥ measured under these conditions (with solutions in both capillaries at concentration c accurately gives the quantity t¥ = 104 / (1 +w¥). The capillaries are filled with the “top” and “bottom” solutions, which are then allowed to diffuse into the “bulk” solution. Resistance ratio readings are taken at various recorded times, beginning 1000 min after the start of the experiment, to determine the quantity t= 104/(1+w) as t approaches t¥. The diffusion coefficient is evaluated using a linear least-squares procedure to fit the data and, finally, an iterative process is applied using 20 terms of the expansion series of Fick’s second law for the present boundary conditions. The theory developed for the cell has been described previously [5]. Interdiffusion coefficients of potassium chloride [9], magnesium nitrate[10], cobalt chloride[11] and beryllium sulphate[12] in water at 298.15 K, and at concentrations from 0.001 to 0.01 mol dm-3, have been measured using a conductimetric cell and an automatic apparatus to follow diffusion. 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. 3. Experimental results and discussion Table 1 shows the estimated percentage of hydrogen ions, z, resulting from the hydrolysis of different ions at different concentrations at 298.15 K, by using the equations (1.8) to (1.9). Table 1 - Estimated percentage of hydrogen ions, z, resulting from the hydrolysis of some cations in aqueous solutions at different concentrations, c, and at 298.15 K, using Eqs (1.8) and (1.9) c/ z% z% z% z% /mol dm-3 (KCl) (Mg(NO3)2) (CoCl2) (BeSO4) 1 x 10-3 3 x 10-3 5 x 10-3 8 x 10-3 1 x 10-2 2 3 2 3 3 -- 1 2 1 1 5 6 8 6 6 -- 69 48 26 34 From the analysis of this table, we see that the diffusion of cobalt ion and mainly beryllium ion are the most clearly affected by their hydrolysis. At the lowest Be2+ ion concentration (3 x 10-3 mol dm-3) the effect of the hydrogen ions on the whole diffusion process has an important and main role (z = 69 %, Table 1). However, we can, to a good approximation, describe these systems as binary if we consider certain facts. For example, in the case of solutions of beryllium sulphate, several studies [12] indicated that the predominant species present are, the solvent, Be2+, SO42- and H+ ions, as well as indicated in the following scheme resulting from hydrolysis of the the Be2+ion. [Be(H2O)4]2+ ↔ [Be(H2O)3(OH)]- + H+ [Be(H2O)3(OH)]- + [Be(H2O)4]2+ ↔ [(H2O)3

Be-OH-Be (H2O)3]3+ However, based on pH measurements (i.e., 2.9 ≤ pH ≤ 3.9) for various BeSO4 solutions at concentrations ranging from 3 x 10-3 mol dm-3 and 1 x 10-2 mol dm-3, and from the low equilibria constants relative to the hydrolysis of the the Be2+ion [15], we can then treat this system as being a binary system. Moreover, given the uniformity of the concentration gradient imposed by our method, it is considered that the value of the diffusion coefficient, which is given to the scientific community, is a quantitative measure of all existing species that diffuse. Concerning the other electrolytes (KCl and Mg(NO3)2), [9,10] the reasonable agreement obtained between the calculated and the experimental values of diffusion coefficient, should result in negligible percentages for the hydronium ion (Table 1). 4. Conclusions We have estimated the percentages of H3O+ (aq) resulting from the hydrolysis of some ions (i.e, beryllium, cobalt, potassium and magnesium ions), using a new model and the experimental and calculated mutual diffusion coefficients for potassium chloride, magnesium nitrate, cobalt chloride and beryllium sulphate in aqueous solutions, contributing in this way for a better knowledge of the structure of these systems. Among the cited systems, we concluded that the diffusion of beryllium sulphate is clearly the most affected by the beryllium ion hydrolysis. 5. Acknowledgments Financial support of the Coimbra Chemistry Centre from the FCT through project Pest-OE/QUI/UI0313/2014 is gratefully acknowledged.