

The experimental upper absolute errors can be calculated by making the subtraction between the experimental activity coefficients of Table 1 and the mean activity coefficients determined with Table 2 data and the definition of mean activity coefficient. Comparing these errors with the ones calculated from equations (17) and (18) it is found that both are in good agreement. The corresponding tabulations are omitted.

### Conclusion

It is necessary to study in deep the methodology applied in order to determine ionic activity coefficients from the mean ionic activity coefficients of the electrolytes. The hydration numbers are parameters of extraordinary importance for these studies. The literature compiles very much tabulations about  $\gamma_{\pm}$  with sufficient accuracy and precision but this is not the case with the  $h_j$  values where the scattering on the data is very significant even with a same measurement method.

### References

- [1] K.S. Pitzer, *Activity coefficients in electrolyte solutions*, CRC Press, Boca Raton, FL, 1991.
- [2] R.A. Robinson and R.G. Bates, *Anal. Chem.*, 45 (1973) 1666.
- [3] R.A. Robinson and R.G. Bates, *Anal. Chem.*, 45 (1973) 1684.
- [4] M.K. Khoshkbarchi and J.H. Vera, *Fluid Phase Equilibria*, 121 (1996) 253.
- [5] M. M. Marcos-Arroyo, M. K. Khoshkbarchi and J. H. Vera, *J. Solution Chemistry*, 25 (1996) 983.
- [6] E. Glueckauf, *Trans. Faraday Soc.*, 51 (1955) 1235.
- [7] D.E. Goldsack, R. Franchetto and A. Franchetto, *Can. J. Chem.*, 58 (1976) 2953.
- [8] P.R. Mussini, P. Longhi, T. Mussini and S. Rondinini, *J. Appl. Electrochem.*, 20 (1990) 645.
- [9] P. Longhi, P.R. Mussini, G. Perboni and S. Rondinini, *J. Solution Chem.*, 24 (1995) 311.
- [10] P.R. Mussini, F. Dandrea, A. Galli, P. Longhi and S. Rondinini, *J. Appl. Electrochem.*, 20 (1990) 651.
- [11] R. Dorta-Rodríguez, *Tesis Doctoral*, Universidad de La Laguna, 2001.
- [12] Y. Marcus, *Ion Solvation*, John Wiley, New York, 1985.
- [13] B.P. Demidovich and I.A. Maron, *Cálculo numérico fundamental*, Paraninfo, Madrid, 1988.

## STUDY OF THE REDUCTION OF MALEIC ACID BY ELECTROCHEMICAL SEMIINTEGRAL TECHNIQUES.

M. Barrera-Niebla\*, M. Pérez-Sánchez and M. González-Morín.  
*Dpto. de Química Física. Universidad de La Laguna. LA LAGUNA. TENERIFE. ISLAS CANARIAS.*

### Abstract

The reduction of maleic acid at a spherical mercury electrode from solutions containing  $1 \text{ mol}\cdot\text{m}^{-3}$  acid has been studied at  $25^\circ\text{C}$ . The pH of solutions was controlled to 2.2 with Britton-Robinson buffer and ionic strength was adjusted with  $500 \text{ mol}\cdot\text{m}^{-3}$  NaCl. The electrochemical semiintegral methods have been employed for the data processing. The derivation of i-q-m-t equations was made following the procedure used by Oldham in the case of planar electrodes. The diffusion coefficients of each component of O/R couple have been considered to share a common value D. The mathematical methods used were those of the semicalculus.

*Keywords:* semiintegral methods, quasi-reversible reactions, maleic acid.

### Introduction

There are very much electrochemical studies about the maleic acid, but in the paper now reported, we pay attention to the references [1-3]. These papers have been analysed to fix the composition of the solutions where the reduction of maleic acid take place, essentially, as a quasi-reversible simple electrode reaction. It must be underlined that the theoretical derivations are made for this type of mechanism occurring at a spherical electrode.

The K.B. Oldham's paper [4] is the basis of the present paper. Also based in his paper, we have published yet another work for the totally irreversible simple electrode reaction case [5]. The mathematical methods employed are based in the fractional calculus [6,7].

We started with the i-t equation reported by K.B. Oldham [8] and the corresponding q-t equation for  $D_O = D_R$  case of a quasi-reversible reduction. The methods of the semicalculus were applied to both equations.

\*Author to whom correspondence should be addressed.

**Experimental**

All chemicals used were Merck "pro analysi". A three electrode cell and a HMDE from Metrohm were used; a SSCE (Ingold) and a platinum grid (SEMPSA) were used as reference and counter electrodes. The electrode area was determined by collecting and weighing fifty drops and the calculation was made under the hypothesis of sphericity for the drops. The temperature of the cell was controlled by a Heto Hetofrig cooling bath. The pH of the solutions was monitored with a glass electrode and a Radiometer pH-meter.

The chronocoulometric measurements were performed by a modular system, namely, (i) a PARC 175 Universal Programmer, (ii) a Digital Nicolet Oscilloscope 3091, (iii) a Potentiostat with coulometer Belpont and (iv) Digital Keithley Voltmeter 179.

The q-t curves were recorded at several potentials. The solutions were prepared with and without electroactive species.

**Results and Discussion**

**Theoretical Results**

The starting point was the Bond and Oldham report [8] and we used their equation (25) for the current-time relationship at a potentiostatted electrode. This equation correspond to the  $D_O = D_R$  case. The charge-time relationship was derived by

$$q(t) = \int_0^t i(\tau) d\tau \tag{1}$$

$\tau$  being a dummy variable.

The application of the fractional calculus to the i-t and q-t relationships let us to obtain the following equations:

$$i - fm = \lambda(fq - m) \tag{2}$$

$$i + \lambda m = i_0 f_i(t) \tag{3}$$

$$m + \lambda q = i_0 f_q(t) \tag{4}$$

where

$$f = \frac{f_i(t)}{\frac{d^{-1/2}}{dt^{-1/2}} f_i(t)} = \frac{d^{1/2}}{dt^{1/2}} \frac{f_q(t)}{f_q(t)} \tag{5}$$

$$f_i(t) = \frac{2}{a} \sqrt{\frac{D}{\pi}} \sqrt{t} + 1 \tag{6}$$

$$f_q(t) = \frac{\sqrt{D}}{a} t + \frac{2}{\sqrt{\pi}} \sqrt{t} \tag{7}$$

$$i_0 = nFAc^b k_f \tag{8}$$

$$\lambda = \frac{k_f + k_b}{D} + \frac{1}{a} \tag{9}$$

"m" being the semiintegral of the faradaic current ( $A \cdot s^{1/2}$ ) or the semidifferential of faradaic charge [4,9]; D is the diffusion coefficient ( $m^2 \cdot s^{-1}$ ); a is the radius of the spherical electrode (m);  $k_f$  and  $k_b$  are the heterogeneous rate constants for the reduction and oxidation reaction, respectively ( $m \cdot s^{-1}$ ); t, i, q are the electrolysis time, and faradaic current and charge, respectively (s, A, C);  $c^b$  is the bulk concentration of electroactive species ( $mol \cdot m^{-3}$ ); n is the number of electrons transferred; F is the Faraday's constant ( $96485.3 C \cdot mol^{-1}$ ) and A is the electrode area ( $m^2$ ). The  $f_i(t)$ ,  $f_q(t)$  and f functions can be calculated for each electrolysis time if we known the diffusion coefficient and the radius of spherical electrode. Equations (2-4) are suitable for carry out linear and non linear regression analysis to obtain the  $i_0$  and  $\lambda$  parameters and from them the heterogeneous rate constants  $k_f$  and  $k_b$ . Then, the analysis of the  $\ln k_f$  versus E and  $\ln k_b$  versus E plots let us to obtain the reductive and oxidative transfer coefficients, respectively.

**Experimental Results**

Figure 1 collects the experimental chronocoulometric curves for potentials ranging from values where the faradaic charge is not very different to nonfaradaic (-0.64, -0.65 V versus SSCE) to values corresponding to the diffusion controlled charge (-0.8, -0.9 V versus SSCE). Using the data of the last two q-t curves in the q versus  $t^{1/2}$  dependence, we obtain an average value for the diffusion coefficient of the oxidised form of  $1.1 \cdot 10^{-9} m^2 \cdot s^{-1}$ . The diffusion coefficient of the reduced form is considered equal to that of the oxidised form. The area of the spherical electrode was  $3.2 \cdot 10^{-6} m^2$ .

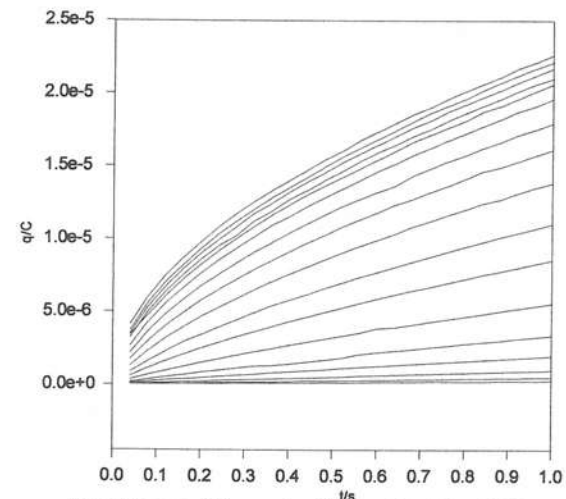


Figure 1. Experimental chronocoulometric curves. Potentials vs SSCE (bottom to top) range from -0.64V to -0.78V step -0.01V. The potentials of the last two curves are -0.8V and -0.9V.

**Discussion**

Figure 2 shows the  $\ln k_f$  versus  $E$  and  $\ln k_b$  versus  $E$  plots. The rate constants were obtained by non linear regression analysis of the experimental data to the theoretical equations.

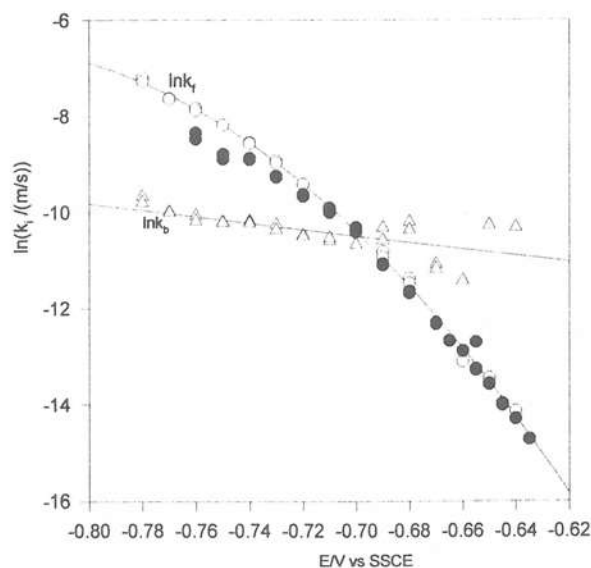


Figure 2. Heterogeneous rate constants-potential dependence.

The bold circles in the figure are point corresponding to  $k_f$  data obtained using two methods developed in our laboratory [10,11]. They are based in a approximate formulation of the Koutecky's function and use polarographic i-t curves as experimental data. The agreement with the data obtained with the method now reported is good. The curvature of the  $\ln k_f$  versus  $E$  plot could be due to the following causes, namely, a Frumkin effect, a potential dependence of the cathodic transfer coefficient following to Marcus or a more complex mechanism. Now, the  $\ln k_b$  versus  $E$  plot shows a variation opposite to the expected one. Likewise, in this moment we communicate a characteristic of the morphology of the q-t experimental data and that it is not showed in the Figure 1, namely, the charge in the reversal step (anodic direction) was nearly constant and equal to the value at the reversal time. This indicates that the reduction product undergo a effective conversion into a non electroactive species which can not be re-oxidised [12]. Hence, the  $\lambda$  parameter obtained by regression must have a different meaning to that defined in equation (9) unless at potentials closed to standard potential. Thus, from data in Figure 2, for example with the  $k_f$  and  $k_b$  values for  $E = -0.69V$  and using the formula valid if it is supposed that the diffusion coefficients of O and R are equal:

$$\frac{k_f}{k_b} = \exp\left\{\left(\frac{-nF}{RT}\right)(E - E_{1/2}^r)\right\} \quad (10)$$

we calculate for  $E_{1/2}^r$  a value of  $-0.693$  V vs SSCE, that agree with that obtained by polarographic techniques [10,11]. Likewise, we have calculated the q-t curve for  $E = -0.69V$  with the above mentioned rate constants. The suitable q-t equation was derived by integration, according to equation (1), of the corresponding i-t equation reported in paper [8] for quasi-reversible E mechanism when  $D_O = D_R$ . The results are collected, together with the experimental data, in Table 1. The agree between experimental and calculated charge is good.

Table 1. Experimental and calculated q-t curve for  $E = -0.69V$  versus SSCE at 25°C.

$t/s$	$10^6 q_{exp}/C$	$10^6 q_{cal}/C$	$t/s$	$10^6 q_{exp}/C$	$10^6 q_{cal}/C$
0.04	0.339	0.352	0.56	3.510	3.502
0.08	0.655	0.663	0.60	3.830	3.701
0.12	0.948	0.952	0.64	3.900	3.896
0.16	1.220	1.226	0.68	4.090	4.089
0.20	1.490	1.487	0.72	4.280	4.278
0.24	1.740	1.738	0.76	4.470	4.463
0.28	1.980	1.980	0.80	4.660	4.647
0.32	2.210	2.214	0.84	4.830	4.827
0.36	2.440	2.442	0.88	5.020	5.006
0.40	2.670	2.664	0.92	5.190	5.181
0.44	2.880	2.880	0.96	5.360	5.355
0.48	3.100	3.092	1.00	5.540	5.526
0.52	3.310	3.299	-----	-----	-----

**Conclusion**

The determination in a separate way of  $k_f$  and  $k_b$  altogether with the study of their variations with the potential has been proved useful to confirm some characteristics of the electrode process such as the chemical reaction experimented by the reduced form of the couple. Finally, it must be underlined that the chosen approach for maleic acid reduction was to consider this electrode process as a simple one. In a further report a more complex mechanism will be tested

**References**

- [1] L. Pospisil and J. Kuta, *Collection Czechoslov. Chem. Commun.*, 34 (1969) 742.
- [2] J.J. Ruiz and J.L. Avila, *Anales de Química*, 76 (1980) 188.
- [3] V.J. Gurjar and I.M. Sharma, *Journal of Applied Electrochem.*, 19 (1989) 113.
- [4] K.B. Oldham, *Journal of Electroanal. Chem.*, 145 (1983) 9.

- [5] M. González-Morín, M. Barrera-Niebla and M. Pérez-Sánchez, *Journal of Electroanalytical Chemistry*, 411 (1996) 1.
- [6] K.B. Oldham and J. Spanier, *The Fractional Calculus*, Academic Press, New York (1974).
- [7] J. Spanier and K.B. Oldham, *An Atlas of Functions*, Hemisphere, Washington, DC, and Springer, Berlin (1987).
- [8] A.M. Bond and K.B. Oldham, *J. Electroanal. Chem.*, 158 (1983) 193.
- [9] K. B. Oldham and J. C. Myland, *Fundamentals of Electrochemical Science*, Academic Press, San Diego (1994).
- [10] M. González-Morín, *Tesina de Licenciatura*, Universidad de La Laguna, 1993.
- [11] M. Barrera-Niebla, M. González-Morín and M. Pérez-Sánchez, *An. Quím.*, 89 (1993) 493.
- [12] A.J.Bard and L.R.Faulkner, *Electrochemical Methods*, John Wiley and Sons, 1980.

## Application of Karl Fischer's Method to materials that only release water at high temperatures

Marta E. Themudo<sup>1</sup>, Aquiles A Barros<sup>2</sup> and Margarida Bastos<sup>2</sup>

<sup>1</sup> Laboratório do Instituto Geológico e Mineiro  
Rua da Amieira, 4465 S. Mamede Infesta codex, Portugal  
([marta.themudo@ign.pt](mailto:marta.themudo@ign.pt))

<sup>2</sup> Centro de investigação em Química U.P.  
Rua do Campo Alegre, 687, 4169-007 Porto, Portugal  
([ajbarros@fc.up.pt](mailto:ajbarros@fc.up.pt))  
([mbastos@fc.up.pt](mailto:mbastos@fc.up.pt))

### Abstract

The present work describes the development of a new experimental set-up to allow determination of water in solid materials that can not be analysed by the traditional Karl Fischer's coulometric titration, as they are not soluble in Karl Fischer's solution and they only release water at high temperatures.

For this purpose, a new tubular oven was designed and tested, where the temperature can be raised up to 1000 °C, which can be coupled to a Karl Fischer Coulometer. Different geological samples were tested, and the results were crossed with other traditionally used methods for this type of determinations.

### Introduction

The determination of the water content of some materials is very important, both from the point of view of their production and commercialisation and for the study and characterization of their chemical and physical properties.

The present work focus water determination in different geological materials. The traditional method for the determination of the total water content in rocks is the Penfield's Method [1]. Nevertheless, it is considered a method of low precision and low accuracy, as it is biased by other volatile components of the sample, that will be treated as water by the method.