

## Thermal characteristics of a cell employed for the anodic oxidation of certain naphthalene derivatives

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### Abstract

The application of a non-linear lumped-parameter thermal balance to the experimental temperature/time profile is shown for the electro-oxidation of 2-methylnaphthalene.

### List of symbols

$A$	Heat loss area (cm <sup>2</sup> ); $A_e$ evaporation area
$C_a$	Thermal capacity (J K <sup>-1</sup> )
$F$	Faraday's constant (96488 C mol <sup>-1</sup> )
$I$	Current (A); $I_m$ Mean current
$(I^2R)_m$	Mean value of Joule heat (W)
LPBE	Acronym for lumped parameter batch electrolyzer
$m$	Mean rate of solvent evaporation (g min <sup>-1</sup> cm <sup>-2</sup> )
$Q_e$	Heat loss rate due to evaporation (W)
$R$	Electrolyte resistance (ohm)
$r^2$	Coefficient of determination for a statistical regression (–)
SSE	Acronym for sum of the squared errors
$T$	Anolyte temperature (°C or K); $T_A$ Ambient temperature; $T_0$ Initial anolyte temperature;
$t$	Time (min)
$U$	Overall heat loss coefficient (W cm <sup>-2</sup> °C <sup>-1</sup> )
$\Delta H_R$	Heat of electrode reaction (J mol <sup>-1</sup> )
$\Delta H_v$	Heat of solvent evaporation (J g <sup>-1</sup> )

### 1. Introduction

The electrochemical oxidation of naphthalene derivatives requires temperatures in the 40–60 °C range, hence a relatively large Joule heat input is necessary, which also has to compensate for partial evaporation of the organic solvent (acetone), and heat loss through the cell boundaries to the ambient [1, 2]. It is shown in this paper that, in spite of inherent complexities in establishing a rigorous heat balance, the increase in cell temperature with time past an initial period of electrolysis can be approximated reasonably well by a lumped parameter heat transport model, for the estimation of mean solvent evaporation rates. Such information is

potentially useful for the design of a medium- and large-scale electro-oxidation process, in contrast to small-scale cells [3].

### 2. Experimental

Experiments were carried out in a double-compartment cylindrical cell utilized for preliminary investigations by Łobuzińska, leading to an advanced research project [4]. Figure 1 shows a sketch of the cell, in which the lower portion of the 2.3 cm dia cathode compartment and the 4.7 cm dia, 9 cm tall anode compartment were joined (at about middle-height) by a 3.5 cm long, 1.6 cm dia cylindrical conduit containing a 2 mm wide porous glass diaphragm at its centre. The electrolytes were made up of a 1:1 (v/v) acetone-aqueous mixture of 0.1 M sodium sulfate, 0.02 M cobalt(II) sulfate, and 0.01 M organics, e.g. 2-methylnaphthalene, 2-ethylnaphthalene and 1-ethylnaphthalene, in an active electrolyte volume of 50 cm<sup>3</sup>. A 0.8 mm dia spiral platinum wire cathode served for proton discharge, and a 1.8 cm dia cylindrical platinum grid anode, with an active surface area of about 27 cm<sup>2</sup>, was employed for the oxidation of the naphthalene derivatives accompanied by oxygen evolution.

The temperature of the magnetically stirred electrolyte was brought to 26 °C prior to electrolysis. A gradual increase in current was effected by the ZT-980-4 Unitra-Unima (Warsaw) voltage-current stabilizer/adaptor, employed for electrolysis. The anolyte temperature was monitored by a thermometer until no further change with time was observed. The ambient temperature remained a constant 20 °C. Although the top of the anode compartment was covered with aluminum foil to contain acetone evaporation, the anolyte level had to be maintained by adding fresh acetone periodically. The anolyte pH gradually decreased from its initial value of 7 during electrolysis.

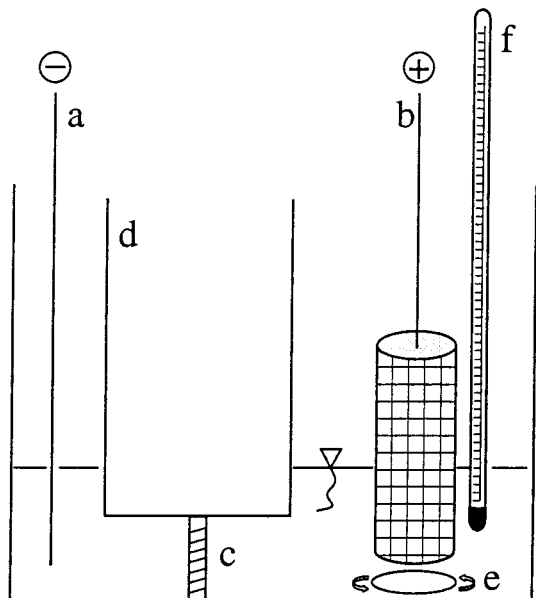


Fig. 1. Schematic of the experimental cell. (a) Pt wire cathode mounted in glass; (b) cylindrical Pt grid anode; (c) porous glass diaphragm; (d) diaphragm support; (e) magnetic stirrer; (f) thermometer.

### 3. Analysis of thermal behaviour

#### 3.1. Application of a lumped parameter batch electrolyzer (LPBE) model

Without the use of this specific acronym, the development of the thermal LPBE model has been amply described in the literature [e.g. 5–9]. Assuming temperature-independent physical parameters within the experimental range, the thermal balance for the anolyte can be written as

$$C_a \frac{dT}{dt} = I^2 R - \frac{I \Delta H_R}{zF} - UA(T - T_A) - Q_e \quad (1)$$

where the last term assigns a constant thermal loss due to acetone evaporation, by means of a mean evaporation rate as an approximation to the experimental partial depletion/replenishment conditions. Since current varies throughout an experiment, Equation 1 is inherently nonlinear, unless the Joule heat term is represented by an averaged value  $(I^2 R)_m$ , to create a linear approximation. Equation 1 implies that the secondary Soret and Dufour effect [10, 11], contact resistance effects, *etc.* are negligible with respect to other heat transport modes.

A realistic numerical value of the overall specific thermal loss rate ( $UA$ ) can be obtained if the initially high temperature is allowed to drop over a sufficiently long time without electrolysis. Equation 1 is simplified to

$$C_a \frac{dT}{dt} \cong -UA(T - T_A) \quad (2)$$

and the slope of its analytical solution

$$\ln(T - T_A) = \ln(T_0 - T_A) - \frac{UA}{C_a} t \quad (3)$$

yields  $U$ . In this manner, cumbersome and presumably unreliable estimations of the convective and radiative transport kinetics based on standard heat transport data compilations are avoided [12].

#### 3.2. Numerical illustration: the electro-oxidation of 2-methylnaphthalene

Table 1 portrays typical experimental observations (Columns 1–3), and predicted temperatures (Column 4 and 5). The mean acetone evaporation rate was established via parametric fitting of  $m$  with physical parameters  $C_a=211.5 \text{ J } ^\circ\text{C}^{-1}$ ;  $\Delta H_R=285.953 \text{ kJ mol}^{-1}$ ;  $\Delta H_v=501.051 \text{ J g}^{-1}$  acetone adopted from the literature [13].

Table 1. Experimental and model-predicted evolution of anolyte temperature during the electro-oxidation of 2-methylnaphthalene

$t$ /min	$I$ /mA	$T$ / $^\circ\text{C}$ (experimental)	$T$ / $^\circ\text{C}$ ; Equation 1; $m = 0.0315$	$T$ / $^\circ\text{C}$ ; Equation 5; $m = 0.0191$
0	45.0	26.0	26.0	26.0
15	88.0	28.5	39.0	39.0
30	119.8	35.5	41.3	43.1
45	122.8	42.0	42.1	44.4
60	124.0	44.0	42.7	44.8
75	123.5	44.0	43.2	44.9
90	123.7	43.0	43.8	45.0
105	129.2	44.0	44.3	45.0
120	130.5	45.0	44.9	45.0
135	132.0	45.0	44.9	45.0
150	132.1	45.0	44.9	45.0

$$R = 4976.413 - 13.5721T \text{ (ohm)}; [T] = \text{K}; r^2 = 0.98$$

$$I = 0.1202 + 1.052 \cdot 10^{-4}(t - 30) \text{ (A)}; [t] = \text{min}; r^2 = 0.91$$

$$Q_e = A_e m \Delta H_v = 144.88m \text{ (W)}$$

$$\text{Equation 1: } dT/dt = 0.2837I^2R - 0.42039I - 0.0773(T - 293) - 41.1024m \text{ (K min}^{-1}\text{)}; [m] = \text{g cm}^{-2}/\text{min}^{-1}; \text{ solution via [14]; } I_m = 0.1156 \text{ (A)}; (I^2R)_m = 9.7588 \text{ (W)}$$

$$\text{Equation 5: } T = (328.186 - 531.736m)[1 - \exp(-0.077294t)] + 299 \exp(-0.077294t) \text{ (K min}^{-1}\text{)}; [t] = \text{min}; [m] = \text{g cm}^{-2} \text{ min}^{-1}.$$

The numerical value of  $UA=0.27246 \text{ W } ^\circ\text{C}^{-1}$  was determined from Equation 3 with  $r^2 \approx 1$ , and 95% confidence interval (0.2690; 0.2758), based on experimental  $T/t$  data without passage of current.

Although poorly predicted at small times, the experimentally observed temperature values are closely fit by the LPBE model past about 30 min of electrolysis, as shown by the low residuals ( $SSE = 4.065 \text{ (}^\circ\text{C)}^2$  excluding the  $t=15$  and  $t=30$  min observations). This short time-related discrepancy, found consistently in all experiments, is due to a deliberate exclusion of current values for  $t \leq 30$  from the  $I(t)$  regression, in order to achieve a high  $r^2$  value. Regression analysis based on the full set of  $I/t$  data (a) yield unacceptably low linear and quadratic correlation parameter values, and (b) predict temperatures for  $t > 30$  min which are consistently lower than experimental observations (even in the case of a cubic-polynomial regression with  $r^2 \approx 0.93$ ). A comprehensive nonlinear analysis does not seem warranted in view of the low degree of correlation ( $r^2 \approx 0.45$ ) for a standard power regression.

Column 5 in Table 1 demonstrates that the inviting simplification of Equation 1 to obtain a linear balance

$$C_a \frac{dT}{dt} \cong (I^2R)_m - \frac{I_m \Delta H_R}{zF} - UA(T - T_A) - Q_e \quad (4)$$

solving to

$$T = T_0 \exp\left(-\frac{UA}{C_a}t\right) + \frac{(I^2R)_m - I_m \Delta H_R / zF + UA T_A - Q_e}{UA} \times \left[1 - \exp\left(-\frac{UA}{C_a}t\right)\right] \quad (5)$$

offers a quick analytical approximation to large-time temperatures, ( $SSE=12.21 \text{ (}^\circ\text{C)}^2$ ), excluding the  $t = 15$ , 30 and 45 min observations), but it results in a lower estimate of the mean acetone evaporation rate.

In conclusion, the LPBE model is a useful tool for predicting temperature evolution in well-stirred batch

electrolyzers, and for estimating mean solvent evaporation rates, if employed with adequate caution.

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## References

1. R.E. Sioda and B. Frankowska, *J. Electroanal. Chem.* **568** (2004) 365.
2. R.E. Sioda, B. Frankowska, A. Łobuzińska and T.Z. Fahidy, *Polish J. Chem.* **78** (2004) 1567.
3. T.Z. Fahidy and R.E. Sioda, *Electrochim. Acta* **49** (2004) 1097.
4. A. Łobuzińska, 'Badanie nad anodowym utlenianiem naftalenu i monoetylnaftalenów (Investigation of anodic oxidation of naphthalene and monoethylnaphthalenes)', M. Sc. Thesis, (University of Podlasie, Siedlce, Poland 2003).
5. D.J. Pickett, 'Electrochemical Reactor Design', (Elsevier, Amsterdam, 1977), Section 6.13, pp. 355–359.
6. T.Z. Fahidy, 'Principles of Electrochemical Reactor Analysis', (Elsevier, Amsterdam, 1985), Chapter 5, pp. 110–136.
7. K. Scott, 'Electrochemical Reactor Engineering' (Academic Press, London, 1991), Section 8.1.3, pp. 478–485.
8. T.Z. Fahidy, *J. Appl. Electrochem.* **16** (1986) 250.
9. R.E. Sioda and T.Z. Fahidy, *J. Appl. Electrochem.* **22** (1992) 347.
10. R. Haase, 'Thermodynamics of Irreversible Processes', (Dover, New York 1969), Section 4.26, pp. 355–356.
11. S.R. deGroot and P. Mazur, 'Non-Equilibrium Thermodynamics', (Dover, New York 1984), Section XI.7, pp. 273–275.
12. R.E. Sioda, *Bull. Electrochem.* **5** (1989) 902.
13. J.A. Dean (Ed.), Lange's 'Handbook of Chemistry', 13th edn, (McGraw Hill, New York, 1985) Table 9.1, p. 9–27; Table 9.4, p. 9–142.
14. E.-Z. Solve, 'The Engineer's Equation Solving and Analysis Tool', (Interpro-Wiley, New York, 1988), Version 1.0.