Modelagem Bromato-Ácido Oxálico-Acetona-Ce(IV)-Ácido Sulfúrico, em fluxo agitado

- Baseado no modelo de Field & Boyd (*J. Phys. Chem.* **1985**, *89*, 3707).
- Integrador numérico escrito por I. Lengyel em Turbo Pascal 6.0 baseado no trabalho de Kaps & Rentrop (*Num. Math.* **1979**, *33*, 55).

Pereira & Faria, *Química Nova*, **2006**, *30*, 541-547.

modelo

- 23 reações (9 reversas)
- 15 espécies independentes
- reação eliminada:

  $2CH_3COCH_2\bullet \Rightarrow CH_3COCH_2CH_2COCH_3$

$Br^- + BrO_3^- + 2H^+ \rightleftarrows HOBr + HBrO_2$
$Br^- + HBrO_2 + H^+ \rightleftarrows 2HOBr$
$Br^- + HOBr + H^+ \rightleftarrows Br_2 + H_2O$
$HBrO_2 + BrO_3^- + H^+ \rightleftarrows 2BrO_2\bullet + H_2O$
$BrO_2\bullet + Ce^{3+} + H^+ \rightleftarrows Ce^{4+} + HBrO_2$
$BrO_2\bullet + (COOH)_2 \rightarrow HBrO_2 + CO_2 + HCO_2\bullet$
$HBrO_2 + HBrO_2 \rightleftarrows HOBr + BrO_3^- + H^+$
$Ce^{4+} + BrO_2\bullet + H_2O \rightleftarrows Ce^{3+} + BrO_3^- + 2H^+$
$HOBr + (COOH)_2 \rightarrow H_2O + CO_2 + HCO_2\bullet + Br\bullet$
$Br\bullet + Br\bullet \rightarrow Br_2$
$HCO_2\bullet + HCO_2\bullet \rightarrow (COOH)_2$

$Ce^{4+} + (COOH)_2 \rightarrow Ce^{3+} + CO_2 + HCO_2\bullet + H^+$
$Ce^{4+} + HCO_2\bullet \rightarrow Ce^{3+} + CO_2 + H^+$
$Br\bullet + (COOH)_2 \rightarrow Br^- + H^+ + HCO_2\bullet + CO_2$
$CH_3COCH_3 + H^+ \rightleftarrows CH_2{=}CHOHCH_3 + H^+$
$CH_2{=}CHOHCH_3 + Br_2 \rightarrow BrCH_2COCH_3 + Br^- + H^+$
$BrO_3^- + (COOH)_2 \rightarrow BrO_2\bullet + H_2O + CO_2 + HCO_2\bullet$
$HOBr + HCO_2\bullet \rightarrow H_2O + Br\bullet + CO_2$
$Br^- + Br_2 \rightleftarrows Br_3^-$
$HCO_2\bullet + H^+ BrO_3^- \rightarrow BrO_2\bullet + CO_2 + H_2O$
$Br_3^- + CH_2{=}CHOHCH_3 \rightarrow BrCH_2COCH_3 + 2Br^- + H^+$
$Br_2 + BrCH_2COCH_3 \rightarrow BrCH_2COCH_2Br + Br^- + H^+$
$Br_3^- + BrCH_2COCH_3 \rightarrow BrCH_2COCH_2Br + 2Br^- + H^+$

REACTIONS	k_f	k_r
$Br^- + BrO_3^- + 2H^+ \rightleftarrows HOBr + HBrO_2$	$5.0\ M^{-3}s^{-1}$	$1.0 \times 10^4\ M^{-1}s^{-1}$
$Br^- + HBrO_2 + H^+ \rightleftarrows 2HOBr$	$2.0 \times 10^9\ M^{-2}s^{-1}$	$5.0 \times 10^{-5}\ M^{-1}s^{-1}$
$Br^- + HOBr + H^+ \rightleftarrows Br_2 + H_2O$	$8.0 \times 10^9\ M^{-2}s^{-1}$	$110\ s^{-1}$
$HBrO_2 + BrO_3^- + H^+ \rightleftarrows 2BrO_2\bullet + H_2O$	$1 \times 10^4\ M^{-2}s^{-1}$	$2.0 \times 10^7\ M^{-1}s^{-1}$
$BrO_2\bullet + Ce^{3+} + H^+ \rightleftarrows Ce^{4+} + HBrO_2$	$7.0 \times 10^4\ M^{-2}s^{-1}$	$8.0 \times 10^5\ M^{-1}s^{-1}$
$BrO_2\bullet + (COOH)_2 \rightarrow HBrO_2 + CO_2 + HCO_2\bullet$	$150\ M^{-1}s^{-1}$	
$HBrO_2 + HBrO_2 \rightleftarrows HOBr + BrO_3^- + H^+$	$4.0 \times 10^7\ M^{-1}s^{-1}$	$2.1 \times 10^{-10}\ M^{-2}s^{-1}$
$Ce^{4+} + BrO_2\bullet + H_2O \rightleftarrows Ce^{3+} + BrO_3^- + 2H^+$	$9.6\ M^{-1}s^{-1}$	$1.3 \times 10^{-4}\ M^{-3}s^{-1}$
$HOBr + (COOH)_2 \rightarrow H_2O + CO_2 + HCO_2\bullet + Br\bullet$	$25\ M^{-1}s^{-1}$	
$Br\bullet + Br\bullet \rightarrow Br_2$	$1.0 \times 10^8\ M^{-1}s^{-1}$	
$HCO_2\bullet + HCO_2\bullet \rightarrow (COOH)_2$	$1.2 \times 10^9\ M^{-1}s^{-1}$	
$Ce^{4+} + (COOH)_2 \rightarrow Ce^{3+} + CO_2 + HCO_2\bullet + H^+$	$27.5\ M^{-1}s^{-1}$	
$Ce^{4+} + HCO_2\bullet \rightarrow Ce^{3+} + CO_2 + H^+$	$1.0 \times 10^6\ M^{-1}s^{-1}$	
$Br\bullet + (COOH)_2 \rightarrow Br^- + H^+ + HCO_2\bullet + CO_2$	$2000\ M^{-1}s^{-1}$	
$CH_3COCH_3 + H^+ \rightleftarrows CH_2{=}CHOHCH_3 + H^+$	$8.3 \times 10^{-5}\ M^{-1}s^{-1}$	$21.3\ M^{-1}s^{-1}$
$CH_2{=}CHOHCH_3 + Br_2 \rightarrow BrCH_2COCH_3 + Br^- + H^+$	$1.03 \times 10^7\ M^{-1}s^{-1}$	
$BrO_3^- + (COOH)_2 \rightarrow BrO_2\bullet + H_2O + CO_2 + HCO_2\bullet$	$5.0 \times 10^{-6}\ M^{-1}s^{-1}$	
$HOBr + HCO_2\bullet \rightarrow H_2O + Br\bullet + CO_2$	$2.0 \times 10^7\ M^{-1}s^{-1}$	
$Br^- + Br_2 \rightleftarrows Br_3^-$	$1.0 \times 10^8\ M^{-1}s^{-1}$	$7.5 \times 10^6\ s^{-1}$
$HCO_2\bullet + H^+ + BrO_3^- \rightarrow BrO_2\bullet + CO_2 + H_2O$	$2.7 \times 10^3\ M^{-2}s^{-1}$	
$Br_3^- + CH_2{=}CHOHCH_3 \rightarrow BrCH_2COCH_3 + 2Br^- + H^+$	$2.8 \times 10^6\ M^{-1}s^{-1}$	
$Br_2 + BrCH_2COCH_3 \rightarrow BrCH_2COCH_2Br + Br^- + H^+$	$5.0 \times 10^{-3}\ M^{-1}s^{-1}$	
$Br_3^- + BrCH_2COCH_3 \rightarrow BrCH_2COCH_2Br + 2Br^- + H^+$	$5.0 \times 10^{-3} M^{-1}s^{-1}$	

Comportamento em

$[H_2SO_4] = 1.0$ M

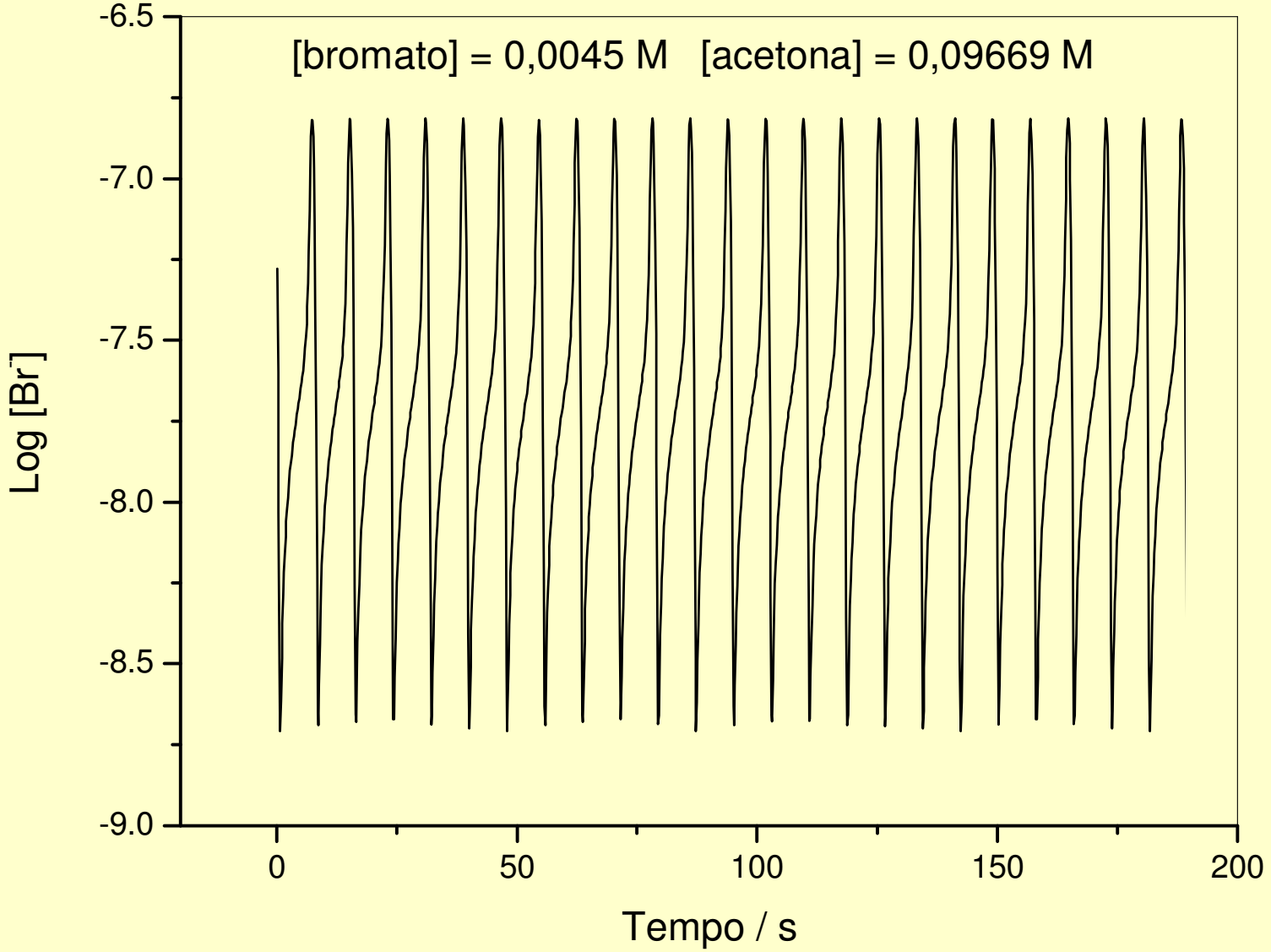
[Ácido Oxálico] = 0,03 M

[Ce(IV)] = 0,0005 M

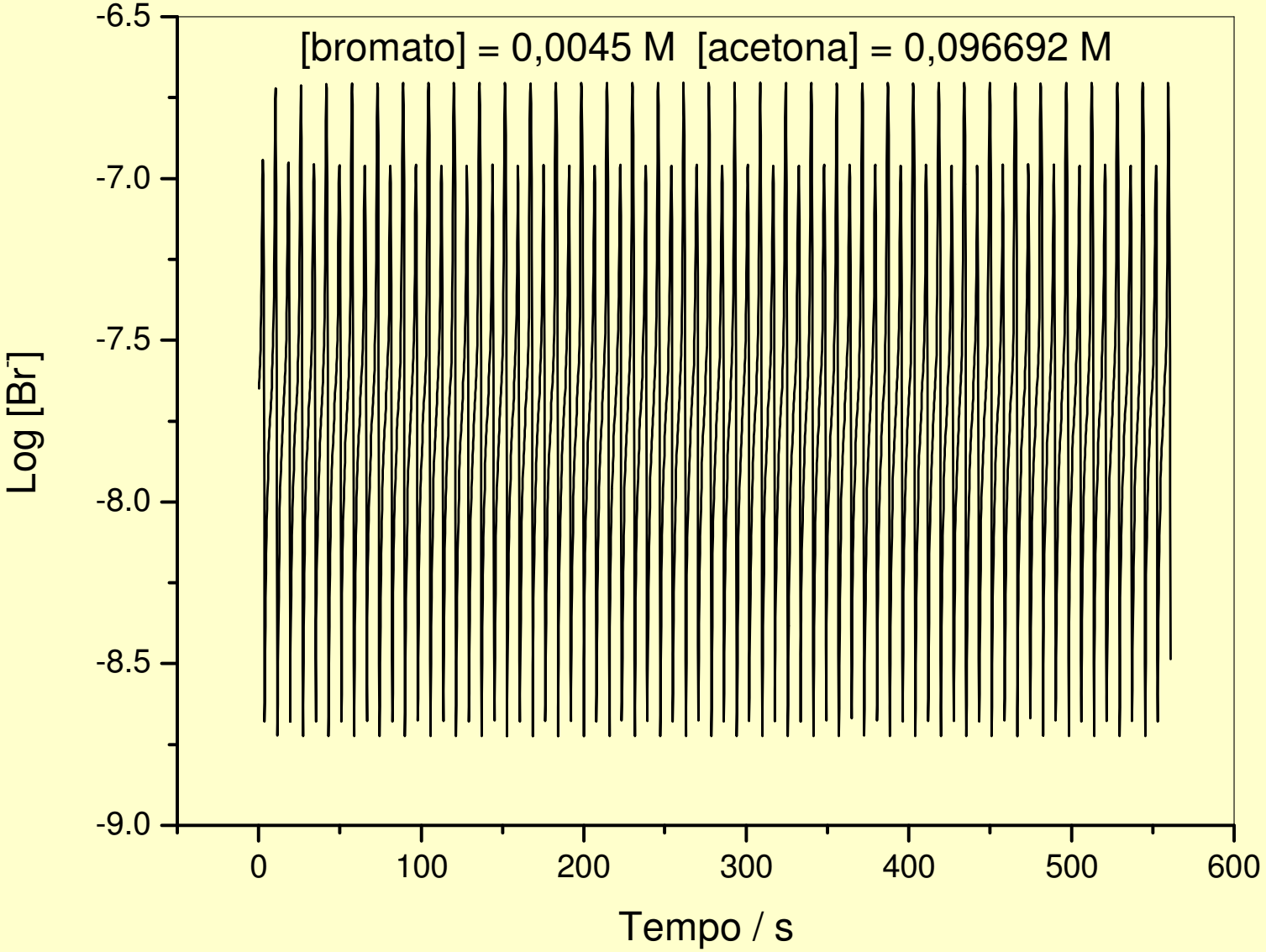
$k_0 = 0{,}005\ s^{-1}$

dobra de período

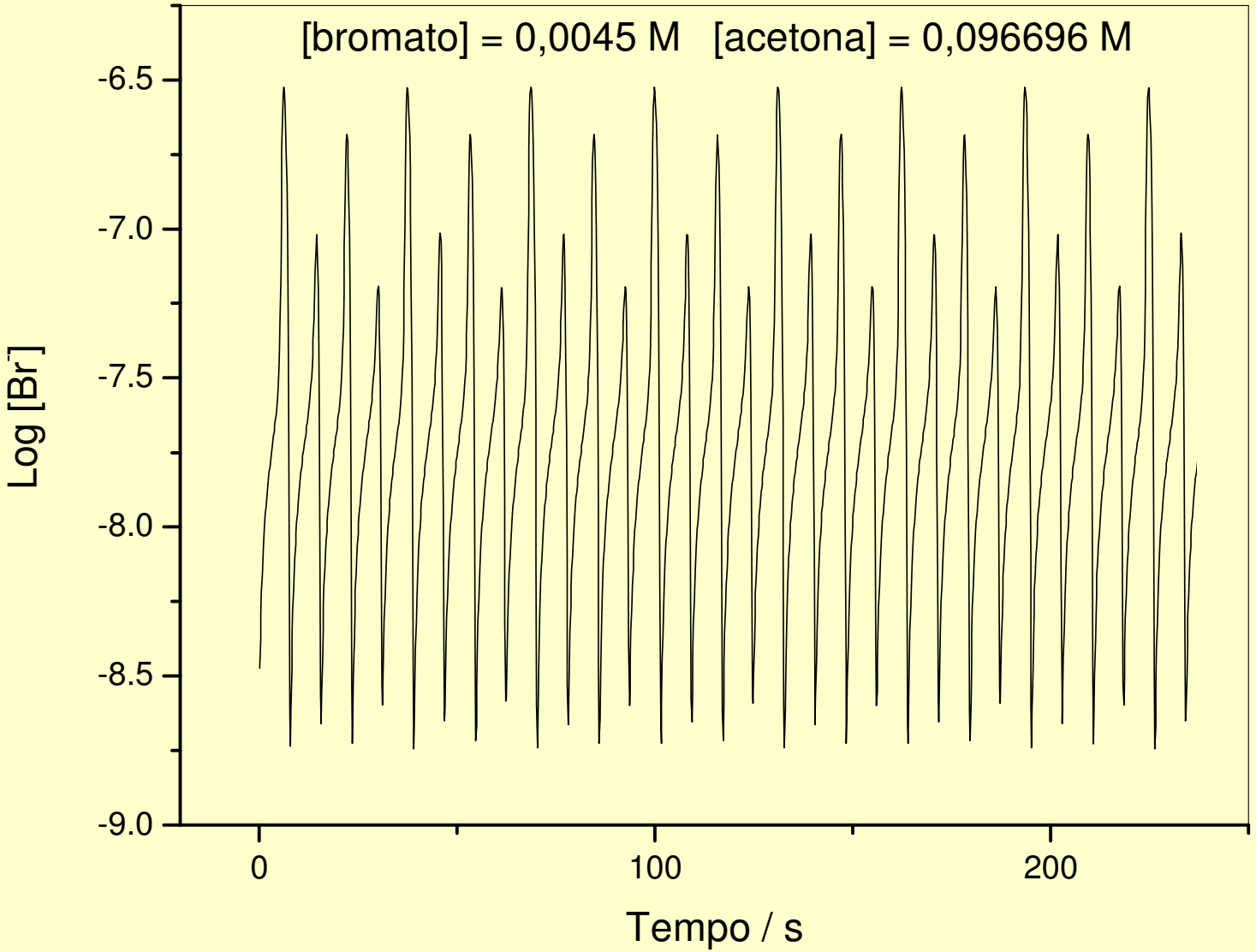
Oscilação de Alta Amplitude (período-1)



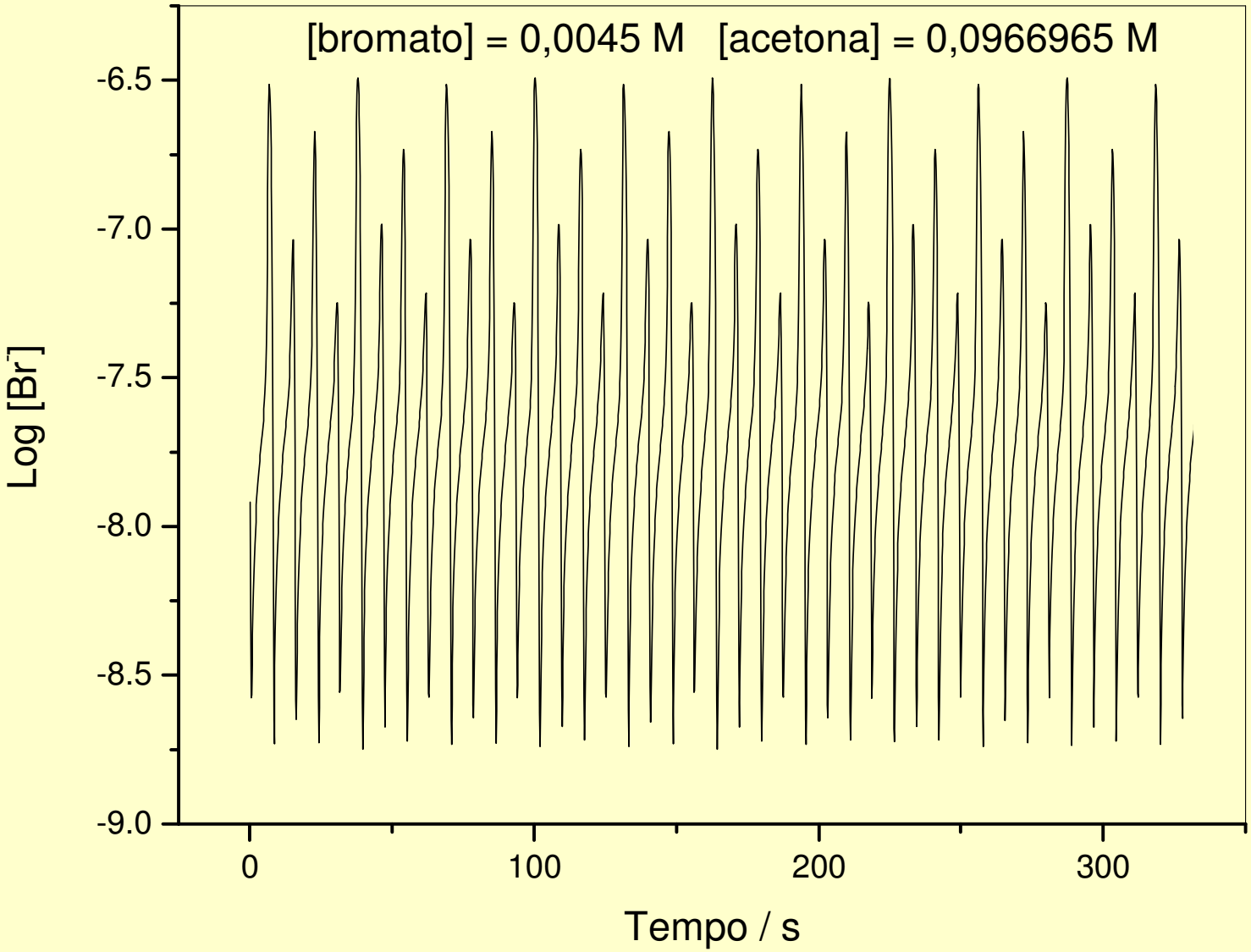
Oscilação de período-2



Oscilação de período-4



Oscilação de período-8



Oscilação de período-16

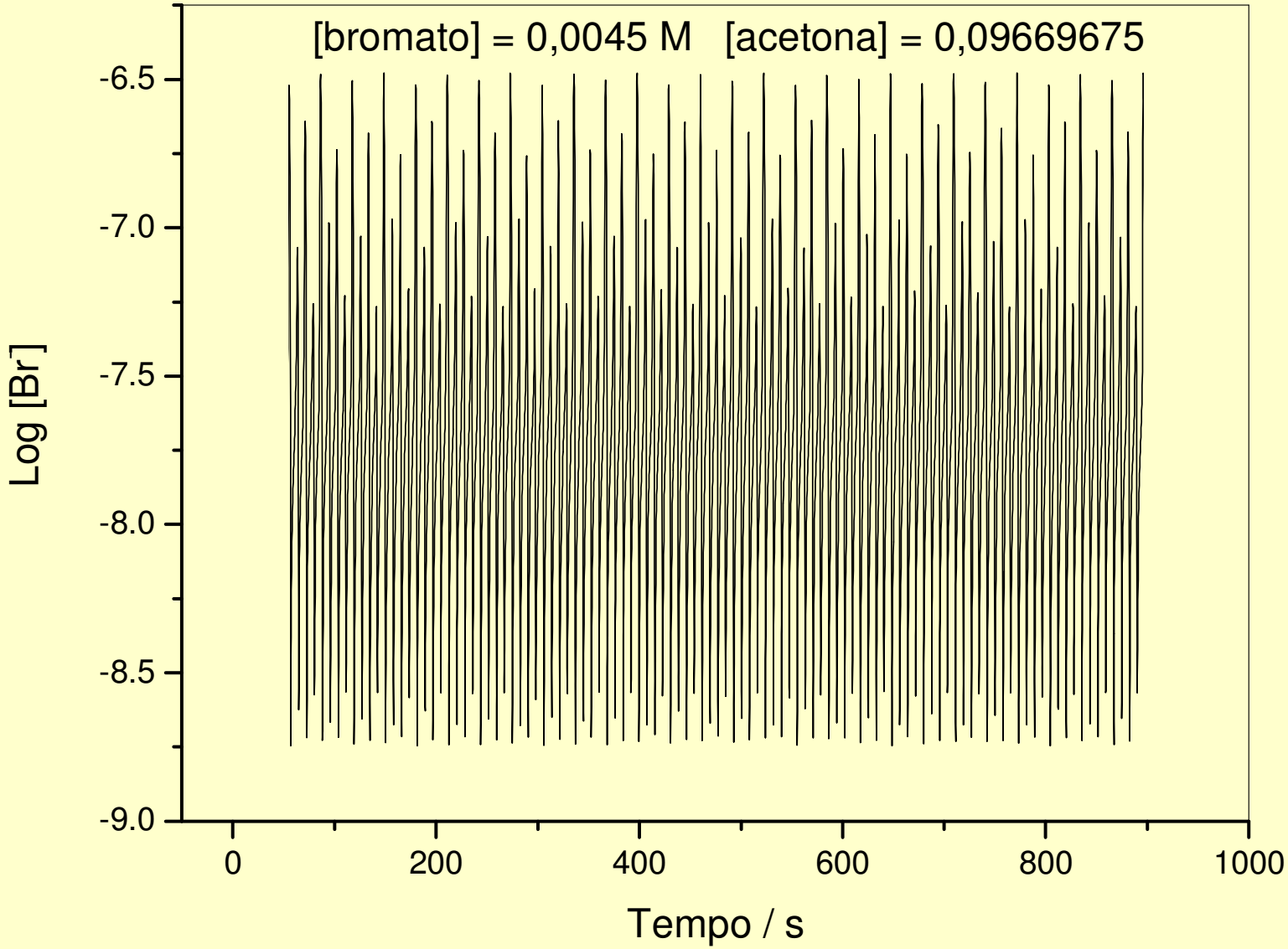
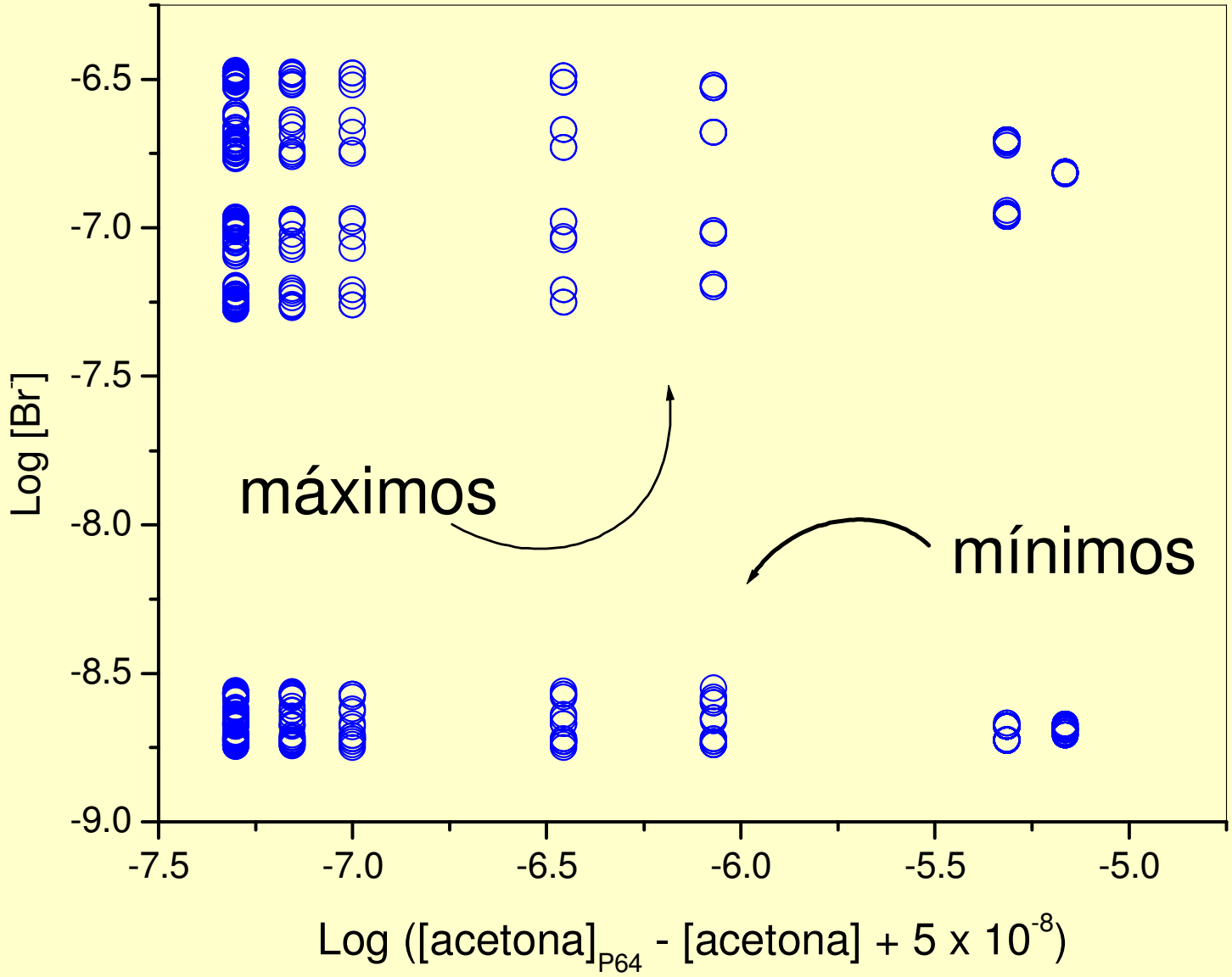


Diagrama de Bifurcações para [bromato] = 0,0045 M



voltar