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Electromigration Oscillations Occurring in Ternary Electrolyte Systems with Complex Eigenmobilities, as Predicted by Theory and Ascertained by Capillary Electrophoresis

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Chemical oscillations are driven by a gradient of chemical potential and can only develop in systems where the substances are far from chemical equilibrium. We have discovered a new analogous type of oscillations in ternary electrolyte mixtures, which we call electromigration oscillations. They appear in liquid solutions of electrolytes and are associated with the electromigration movement of ions when conducting an electric current. These electromigration oscillations are driven by the electric potential gradient, while the system can be close to chemical equilibrium. The unequivocal criterion for the instability of the electrolyte solution and its ability to oscillate is the existence of complex system eigenmobilities. We show how to calculate the system eigenmobilities by utilizing the linear theory of electromigration and how to identify the complex system eigenmobilities to predict electromigration oscillations. To experimentally prove these electromigration oscillations, we employ a commercially available instrument for capillary electrophoresis. The oscillations start a certain period of time after switching on the driving electric current. The axial concentration profiles of the electrolytes in the capillary attain a nearly periodic pattern with a spatial period in the range of 1–4 mm, with almost constant amplitude. This periodic pattern moves in the electric field with mobility that is equal to the real part of the complex eigenmobility pair. We have found several ternary oscillating electrolytes composed of a base and two acids, of which at least one has higher valence than one in absolute value. All the systems have three system eigenmobilities: one is real and close to zero, and the two others form the complex conjugate pair, the real part of which is far from zero.

1. Introduction

Oscillations are well-known phenomena in everyday life, often appearing in mechanical systems or in electric circuits. In these cases, the direction of motion of the object or electric current may be reversed many times with almost constant

amplitude. Such oscillations are used in a vast number of technically important applications. Oscillations in chemical systems, on the other hand, are not that common, since in most cases the evolution of a chemical reaction leads to a monotonic change in the chemical parameters. Chemical oscillations were discovered in the 1960s by Belousov¹ and Zhabotinskii.² They found that the oxidation of analogues of malonic acid by bromate in the presence of cerium ions produced oscillations in the concentration of the reaction constituents, appearing

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spontaneously when carried out in a well-stirred homogeneous medium. When performed in nonmixed vessels, spatial concentration structures were formed. Unlike oscillations in mechanical or electrical systems, chemical oscillatory trajectories cannot pass through a composition where all concentrations simultaneously have equilibrium values. Studies of such chemically oscillating systems have utilized previously developed theories of nonequilibrium thermodynamics and the concepts of open systems, so criteria for evaluating the stability of such systems³ already exist. The oscillating Belousov–Zhabotinskii reaction was an example of a “purely” chemical oscillation appearing even in a well-homogenized environment and has been subsequently thoroughly analyzed,^{4,5} as have been the mechanisms of other chemical oscillation systems.⁶ Sometimes, chemical reactions by themselves do not cause oscillatory behavior but can oscillate when coupled with additional physical processes such as film formation,⁷ heat transfer, or fluid convection.⁸

Recently, we discovered a new type of oscillations which are an analogue of chemical oscillations and which are associated with the electromigration movement of ions in liquid solutions. Unlike chemical oscillations, in which the system is far from chemical equilibrium and the driving force is derived from the chemical potential gradient, these electromigration oscillations are driven by the electric potential gradient, and the system can be close to chemical equilibrium.

Usually, the electromigration of ions in solution is used for the separation of various compounds when they have different velocities in the electric field. This is applied in the use of elegant separation techniques such as electrophoresis. It has been assumed that this type of movement just leads to a possible aperiodic transport of compounds. We found, however, that an aqueous solution of a certain binary electrolyte, sebacic acid/sodium or sebacic acid/imidazole buffer, is unstable when an electric current passes through and that the originally homogeneous buffer solution in the electrophoretic capillary forms periodic spatial concentration structures—or oscillations.⁹ The oscillations in this system are based on a rather exceptional property of sebacic acid (decanedioic acid): the ionic mobility of its divalent form, u_2 ($44.9 \times 10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$), is more than two times higher than the mobility of the monovalent form, u_1 ($20.7 \times 10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$). The ratio u_2/u_1 for sebacic acid is thus 2.17, whereas for most other divalent ions this ratio is less than 2. This rather special property appears in some compounds that significantly change their molecular geometry when swapping from one ionic form to the other.^{10,11} The sebacic acid molecule consists of a long hydrophobic chain with hydrophilic carboxyl groups at both ends, so conformational changes are expected to occur when the dissociation state changes.

We were able to predict and explain the oscillation in the sebacic acid system with a powerful tool—the linear theory of electromigration.^{12–15} We found that for an electromigration system to be nonstable when electric current is applied and to be capable of forming periodic oscillations, the existence of complex system eigenmobilities is an unequivocal criterion. For binary systems, we showed that if the ratio of ionic mobilities of the divalent and monovalent ionic forms, u_2/u_1 , is higher than 2.12, two system eigenmobilities are no longer real but rather form a complex conjugate pair. The real part of the complex pair provides the electrophoretic mobility of the periodic pattern; in the particular case of the systems based on sebacic acid, it was close to zero.

While the oscillations in the binary sebacic buffer system⁹ were a consequence of the rather special behavior of sebacic acid ions in solution, we have found that such oscillations can appear in many more electrolytes than originally supposed, especially in more complex mixtures. In this paper, we present (i) newly found oscillating electromigration systems composed of three constituents that we predicted and analyzed by means of the linear theory of electromigration and (ii) a numerical simulation for the system of electromigration nonlinear dynamic equations allowing a prediction of the amplitude of oscillations.

2. Theoretical Background

2.1. Electrophoretic Matrix M. We introduced the linear theory of electromigration in a previous paper;¹⁴ here, we give a concise overview. As constituents of the electromigration system, we include weak acids or weak bases or ampholytes, both mono- and multivalent. Hydronium and hydroxide ions are not regarded as constituents in the model because their concentrations are given by the ionic product of water and the electroneutrality equation. We consider N constituents of aqueous solutions, though all conclusions also hold for solutions in any protic solvent. The analytical (net) concentration of the i th constituent is denoted by c_i . Any constituent is characterized by two integers, $n_i \leq 0$ and $p_i \geq 0$. The integer z satisfying $n_i \leq z \leq p_i$ is used to denote the ionic (and neutral) forms of the constituent in question. Thus, by $c_{i,z}$ we denote the concentration of the i th constituent with charge z (when $z \neq 0$) and by $c_{i,0}$ the concentration of its neutral form ($z = 0$). For any i , we have $c_i = \sum_{z=n_i}^{p_i} c_{i,z}$. For bases, $n_i = 0$, $p_i > 0$; for acids, $n_i < 0$, $p_i = 0$; and for ampholytic species, $n_i < 0$, $p_i > 0$. Further, to simplify the notation, we use the term hydrogen ions, H^+ , rather than hydronium ions, H_3O^+ , and use the notations c_{H} and c_{OH} to denote the concentration of H^+ and OH^- , respectively. Ionic and neutral forms of the constituents are bound via fast chemical dissociation equilibria. The acid base dissociation constants $K_{i,z}$ relating the ionic forms are defined as

$$K_{i,z+1}c_{i,z+1} = c_{i,z}c_{\text{H}} \quad \text{for } z = 0, 1, \dots, p_i - 1 \quad (1)$$

$$K_{i,z-1}c_{i,z} = c_{i,z-1}c_{\text{H}} \quad \text{for } z = 0, -1, \dots, n_i + 1 \quad (2)$$

$$c_{\text{OH}}c_{\text{H}} = K_{\text{W}} \quad (3)$$

with K_{W} being the ionic product of water.

The electric conductivity of the solution is given by $\kappa = F(\sum_{i=1}^N \sum_{z=n_i}^{p_i} |z| u_{i,z} c_{i,z} + u_{\text{H}} c_{\text{H}} + u_{\text{OH}} c_{\text{OH}})$, where F is the Faraday constant; $u_{i,z}$ is the ionic mobility of the z th ionic form of the i th constituent; and u_{H} and u_{OH} are the mobility of hydrogen and hydroxide ions, respectively. For the description of the system, matrix notation is used: the analytical concentrations of the constituents are represented as a column vector \vec{c} , i.e., $\vec{c} = (c_1, \dots, c_N)^T$, where the superscript T denotes the transpose matrix, so the vector of constituents' concentrations is a column vector. Before the electric current has been applied, the system contains N constituents at certain concentrations $\vec{C} = (C_1, \dots, C_N)^T$ expressing its composition.

We thus analyze the temporal behavior of the constituents distributed almost uniformly in the space, which we regard here as the space inside an electrophoretic capillary. One spatial coordinate, x , along the capillary axis prevails over the perpendicular ones, so we are looking for concentrations $\vec{c}(x, t)$. As a perturbation, we consider a small change of concentrations

in a rather small spatial interval, which can be identified with the injection zone in electrophoresis. The problem can be linearized when adopting the assumption that the perturbations of all constituents' concentrations are small. The perturbation of the original concentrations, $\vec{c}(x,t) = \vec{C} - \vec{c}(x,t)$, can be then found as a solution to the linearized system

$$\frac{\partial \vec{c}}{\partial t} = -\frac{j}{\kappa_0} \mathbf{M} \frac{\partial \vec{c}}{\partial x} \quad (4)$$

where x is the length coordinate in the direction of the outer electric field (in fact, the direction of the capillary axis); t is the time; κ_0 is the conductivity of the undisturbed solution; $j = \kappa_0 E$ is the density of the electric current; $E = -\partial\varphi/\partial x$ is the intensity of the electric field; φ is the electric potential; and \mathbf{M} is a constant Jacobian matrix of type $N \times N$ as described in ref 14; here, we call it the electrophoretic matrix. The initial conditions take the form

$$\vec{c}(x, 0) = \vec{C} + \vec{c}^{\text{in}}(x) \quad (5)$$

where \vec{c}^{in} are initial perturbations of the system, much smaller than any of the concentrations \vec{C} .

Equation 4 is the transport equation expressing the electromigration movement of the constituents under the influence of the electric field (or electric potential gradient). The diffusion motion of ions caused by the chemical potential gradient is neglected here. The elements of matrix \mathbf{M} have the dimension of the electrophoretic mobility. We denote the eigenvalues of the matrix \mathbf{M} by λ_i , $i = 1, \dots, N$, and call them eigenmobilities. Further, we denote a left row eigenvector \vec{q}_i corresponding to the eigenvalue λ_i .

2.2. Real Eigenmobilities. As a matter of fact, in the vast majority of electrophoretic systems all eigenvalues are real and mutually different. Under such conditions, the linear system of equations given by eq 4 can be solved easily. As we showed in ref 14, the matrix \mathbf{Q} constructed of the left eigenvectors enables the transformation of the original system eq 4 to a system with new dependent variables w_1, \dots, w_N , by transformation $\vec{w} = \mathbf{Q}\vec{c}$. When multiplying eq 4 from the left by the matrix \mathbf{Q} , we find that each component $w_k(x,t)$, $k = 1, \dots, N$, of the vector \vec{w} satisfies

$$\frac{\partial w_k(x,t)}{\partial t} = -\frac{j}{\kappa_0} \lambda_k \frac{\partial w_k(x,t)}{\partial x} \quad (6)$$

where for time $t = 0$

$$w_k(x, 0) \equiv w_k^{\text{in}}(x) = \vec{q}_k \vec{c}^{\text{in}} \quad (7)$$

The solution to eq 6 yields a set of traveling waves (or zones)

$$w_k(x,t) = w_k^{\text{in}} \left(x - \frac{j}{\kappa_0} \lambda_k t \right) \quad (8)$$

which move with the velocity $j\kappa_0^{-1}\lambda_k$ along the capillary. These traveling zones form features which are called system zones and which are well-known in electromigration separation methods.

TABLE 1: Composition of Ternary Electrolytes and Calculated System Eigenmobilities Resulting from the Search for Potentially Oscillating Systems Based on Peakmaster Software

system	constituents	calculated concentration [mM]	experimental concentration [mM]	system eigenmobilities [$10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$]
A	GMP ^a	5.000	5.000	0.00
	phosphoric acid	5.000	5.000	-29.70 + 1.16i
	Na ⁺	14.200	14.200	-29.70 - 1.16i
B	maleic acid	4.000	4.000	0.05
	citric acid	1.136	1.136	-44.87 + 0.48i
	Na ⁺	7.129	7.450	-44.87 - 0.48i
C	chromic acid	3.414	4.414	0.01
	phthalic acid	2.734	2.734	-51.08 + 1.74i
	Cs ⁺	9.662	9.662	-51.08 - 1.74i
D	acetic acid	2.152	2.152	0.01
	citric acid	1.906	1.906	-41.86 + 0.56i
	Na ⁺	6.660	6.760	-41.86 - 0.56i
E	maleic acid	3.995	3.995	0.03
	phthalic acid	1.232	1.232	-41.23 + 0.66i
	Na ⁺	7.433	7.533	-41.23 - 0.66i

^a Guanosine 5'-monophosphate.

2.3. Complex Eigenmobilities. We had previously noticed¹² that in capillary electrophoresis the electrophoretic system behaves in an unusual way when the system eigenmobility and the effective mobility of a constituent injected as the analyte are the same. As is already known,¹⁶ coinciding eigenvalues of the Jacobian matrix lead to a resonance solution. In analogy to mechanical or electrical systems, we referred to such a situation as resonance as well.¹² Our next step was to find electromigration systems where two (or more) system eigenmobilities are close enough to "interact"—to form complex coalescence. This idea was supported by the fact that the electrophoretic matrix \mathbf{M} is real and nonsymmetrical, so its eigenvalues can generally be complex numbers. The solution to such systems with complex eigenvalues is no longer a set of traveling waves but has features of spontaneous chaos or oscillations. The analytical solution in a closed form for such a case can be performed by means of Fourier transformation, which we will publish elsewhere. Here, we concentrate on finding and inspecting electromigration systems possessing complex eigenmobilities.

3. Experimental Section

3.1. Chemicals and Instrumentation. Chemicals used as coating materials, marker substances, or buffer constituents (Table 1) were mostly of analytical reagent grade and obtained as follows: guanosine 5'-monophosphate disodium salt (GMP, 99%), sodium dihydrogen phosphate (anhydrous, p.a.), citric acid (monohydrate, p.a.), phthalic acid (p.a.), thiourea (p.a.), hexadimethrin bromid (Polybrene) from Fluka, Switzerland; phosphoric acid (85%) and maleic acid from Lachema, Czech Republic; cesium chromate (99.9+%) and cesium hydroxide (monohydrate, 99.95%) from Sigma-Aldrich, Germany; acetic acid (99%) from Lach-Ner, Czech Republic; 0.1 mM solution of NaOH from Agilent Technologies, Germany; and sodium hydroxide (NaOH 0.1 M Titrisol) from Merck Chemicals, Germany. Water was prepared by a Milli-Q system, Millipore, USA.

Experiments were performed with Agilent^{3D} CE equipment controlled by ChemStation B.01.03 software (Agilent Technologies GmbH, Waldbronn, Germany). A fused silica capillary (50 μm I.D., 365 μm O.D.) was provided by CaCo (Slovakia). The total capillary length and the distance to the detector are given in Table 2. A new capillary was preconditioned by rinsing with distilled water (10 min), followed by 0.1 M NaOH (10 min),

TABLE 2: Composition of the Ternary Systems with Experimentally Confirmed Oscillations^a

system	chemicals	concentration [mM]	capillary lengths	driving voltage [kV]
A	GMP disodium salt	5.000	49.8 cm L_{tot}	-25 kV
	phosphoric acid	0.800	41.4 cm L_{det}	
	NaH ₂ PO ₄	4.200		
B	maleic acid	4.000	50.0 cm L_{tot}	-20 kV
	citric acid	1.136	41.5 cm L_{det}	
	NaOH	7.450		
C	cesium chromate	4.414	50.0 cm L_{tot}	-20 kV
	phthalic acid	2.734	41.5 cm L_{det}	
	CsOH	0.834		
D	acetic acid	2.152	50.3 cm L_{tot}	-20 kV
	citric acid	1.906	41.8 cm L_{detUV}	
	NaOH	6.760	35.3 cm L_{detCCD}	
E	maleic acid	3.995	50.3 cm L_{tot}	-20 kV
	phthalic acid	1.232	41.8 cm L_{det}	
	NaOH	7.533		

^a The selection of the constituents was based on the data given in Table 1.

and again with distilled water (10 min). The capillary was then dynamically coated by a cationic polymer to reverse the electroosmotic flow using the procedure described in ref 17 with the following modifications: activation - rinsing with deionized water for 3 min, with 1 M HCl for 5 min, and with deionized water for 5 min; Polybrene coating - rinsing with 5% w/w aq. Polybrene for 5 min, application of 25 kV for 20 min, rinsing with 5% w/w aq. Polybrene 5 min, and with deionized water for 5 min. Before each measurement, the capillary was flushed with the respective electrolyte solution until the detector baseline was stable. The capillary was thermostatted at 25.0 °C. For detection, a photometric diode array detector (DAD) operating at 214 nm wavelength (if not otherwise stated) was used. In some cases, a contactless conductivity detector (CCD) developed in our laboratory¹⁸ was also used. Samples were injected with 30 mbar of pressure for 5 s. Driving voltage is given in Table 2. Thiourea at a 5 mM concentration served as a neutral UV absorbing EOF marker in all injected samples.

3.2. Software. For the calculation of the system eigenmobilities we used PeakMaster,¹⁵ free software which can be downloaded from our Web site (<http://www.natur.cuni.cz/gas>). Ionic mobilities and pK_a values—input data for the calculation of eigenmobilities—are included in the compound database of PeakMaster, which is based on the data published by Hirokawa.¹⁹ Those data we used for this paper are listed in Table 3. For calculating eigenvalues of the matrix **M**—the system eigenmobilities—PeakMaster utilizes the QR method implemented according to ref 20, which can also calculate complex eigenvalues. To assist finding regions in an electrolyte composition with complex eigenmobilities, we added a new facility to PeakMaster enabling the user to automatically scan the concentration of one or two constituents, to depict such regions

graphically and even to find the composition with the maximum imaginary part of the eigenmobility.

4. Results and Discussion

On the basis of an inspection of numerous electromigration systems by means of PeakMaster, we managed to find new electrolyte mixtures possessing complex system eigenmobilities. The systems are ternary, formed of three constituents: two acids (of which at least one has a valence higher than one) and one base. As the number of system eigenmobilities has to be the same as the number of constituents, all systems have three eigenmobilities: one being close to zero, while the other two coalesce into a complex conjugate pair. Other ternary oscillating systems composed of two bases and one acid or quaternary electrolyte systems will be introduced elsewhere.

To experimentally demonstrate the existence of these oscillations, the same arrangement as is common in capillary electrophoretic separations was chosen. Both electrolyte vessels and the capillary were filled with the electrolyte solution in question. As is usual in fused silica capillaries, silanol groups at the inner surface carry a negative electric charge. Therefore, an electric double layer with a characteristic zeta potential is formed, and electroosmotic flow (EOF) occurs when an electric field is axially applied. To reverse the direction of the EOF, we modified the capillary wall with a cationic polymer by means of a common procedure described in the Experimental Section. In this way, the EOF drove the bulk solution toward the UV detector placed at the anodic side of the capillary. The near zero eigenmobility causes a stationary system peak, which does not move electrophoretically but is pushed by the EOF. The complex system eigenmobilities do not point to an appearance of system zones but cause instability of the solution and the rise of periodic structures, or oscillations, when the electric current passes.

We found numerous oscillating ternary (and more complex) electrolyte systems; here we introduce only several of them. First, we will discuss in detail the behavior of the oscillating system composed of GMP, phosphoric acid, and Na⁺ ions, as a typical example which oscillates very easily and gives nice periodic patterns. Then we will introduce some other ternary systems that behave in an analogous way.

4.1. System A: GMP/Phosphoric Acid/Na⁺. As PeakMaster reveals, the solution of 5.000 mM GMP, 5.000 mM phosphoric acid, and 14.200 mM Na⁺ (which we abbreviate as system A, see Table 1) has three system eigenmobilities: one is close to zero, $0.00 \times 10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$, the other two form a complex conjugate pair of $(-29.70 \pm 1.16i) \times 10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$. As GMP is the only UV absorbing ionic constituent in the solution, the UV detector operating at 214 nm records the GMP concentration profile. To form an initial disturbance in the solution and to determine the velocity of the EOF, we injected a short plug of

TABLE 3: Mobilities and pK_a Values Used as Input Data in the Calculations^a

constituent	u_{+1}	u_{-1}	u_{-2}	u_{-3}	pK_{+1}	pK_{-1}	pK_{-2}	pK_{-3}
acetic acid	-	42.4	-	-	-	4.756	-	-
citric acid	-	28.7	54.7	74.4	-	3.128	4.761	6.396
chromic acid	-	59.3	81.1	-	-	0.745	6.49	-
GMP	-	21.7	38.0	54.3	-	2.845	6.512	9.5
maleic acid	-	41.3	62.4	-	-	1.921	6.225	-
phosphoric acid	-	34.6	61.4	71.5	-	2.16	7.21	12.67
phthalic acid	-	28.1	52.9	-	-	2.95	5.408	-
Cs ⁺	80.1	-	-	-	13	-	-	-
Na ⁺	51.9	-	-	-	13	-	-	-

^a u_z is the mobility of the z th charged form of the constituent. K_z is the corresponding dissociation constant.

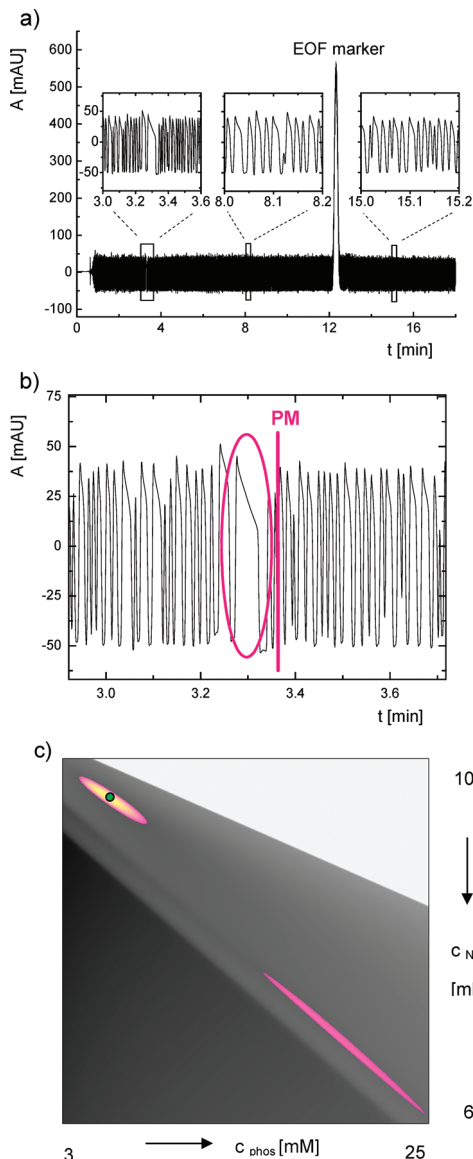


Figure 1. Oscillation system A composed of 5.000 mM GMP, 5.000 mM phosphoric acid, and 14.2 mM Na^+ . (a) Electropherogram recorded by UV absorbance at 214 nm, with three inlays showing the shape of oscillations. A , absorbance; t , time. The peak denoted EOF marker shows the original position of an injected thiourea plug transported to the detector by the EOF. (b) Electropherogram in the expanded time scale. The vertical pink line denoted by PM shows the calculated position corresponding to the real part of the complex system eigenmobility. The real irregularity is bracketed by the ellipse. (c) Depiction of the concentration areas of eigenmobilities in colors for a fixed concentration of GMP of 5.000 mM. C_{phos} and C_{Na^+} are concentrations of phosphoric acid and sodium ions, respectively. The area in yellow–violet comprises compositions with complex eigenmobilities, and areas in various shades of gray comprise compositions with all eigenmobilities real. The composition of the electrolyte experimentally tested is denoted as a green point in the yellow–violet area.

the electrolyte with the same constituents but with a slightly different concentration (10% lower concentration, i.e., 4.75 mM GMP, 4.75 mM phosphoric acid, 13.490 mM Na^+). Moreover, the injected solution also contained a UV absorbing neutral compound, 5 mM thiourea, which served as the EOF marker. It should be pointed out that in fact no disturbance injection is necessary to produce an oscillation.

In Figure 1a, the resulting electropherogram is shown; it can be seen that the system started to oscillate after 0.6 min and continued oscillating with almost constant amplitude (see the

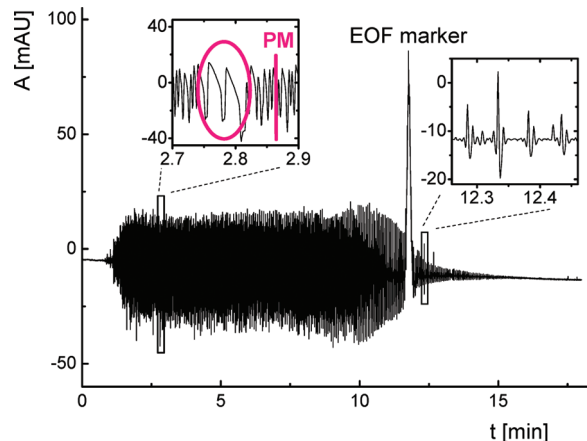


Figure 2. Electropherogram recorded by UV absorbance at 214 nm for oscillation system B: 4.000 mM maleic acid, 1.136 mM citric acid, 7.450 mM Na^+ . For details, see the text and Figure 1.

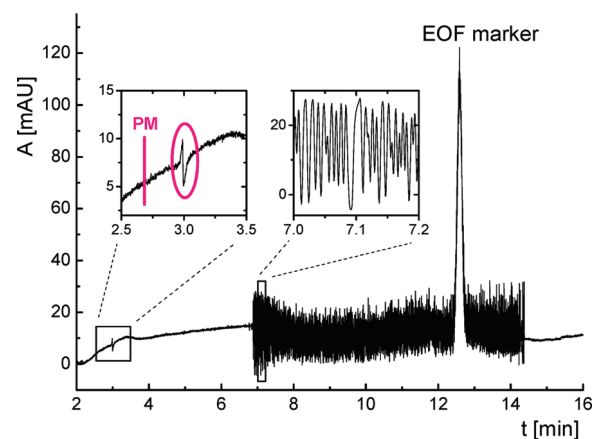


Figure 3. Electropherogram recorded by UV absorbance at 214 nm for oscillation system C: 4.414 mM chromic acid, 2.734 mM phthalic acid, 9.662 Cs^+ . For details, see the text and Figure 1.

inlays depicting some parts of the pattern at a magnified time scale). The thiourea peak at 12.32 min provides a mobility for the EOF of $-11.16 \times 10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$. The electrophoretic mobility of the pattern should be equal to the real part of the complex mobility pair. Unlike the oscillation system with sebacic acid,⁹ here the periodic pattern exhibits relatively fast anionic movement, with mobility of $-29.70 \times 10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$. Indeed, this finding was supported by injecting a small plug of electrolyte with slightly different concentration, forming a disturbance in the originally uniform concentration profiles, and which eventually resulted in a certain irregularity in the periodic pattern. As the movement of all features in the capillary is given by the vectorial sum of the electrophoretic and electroosmotic velocities, the injection irregularity moves (together with the whole oscillation pattern) with the mobility of $-11.16 \times 10^{-9} - 29.70 \times 10^{-9} = -40.86 \times 10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ and should appear (according to PeakMaster) at 3.363 min in the electropherogram. The left-hand inlay in Figure 1a and Figure 1b shows the electropherogram around 3.3 min. In Figure 1b, the theoretically calculated position of the irregularity is shown as a vertical pink line denoted by PM, whereas the experimentally observed irregularity is bracketed by an ellipse. It can be seen that the difference in the positions of calculated and predicted irregularities is as small as about 0.1 min, which confirms well the validity of the theoretical model. The same comparisons of the real and theoretically calculated irregularities are also given in the subsequent figures showing the other oscillation systems.

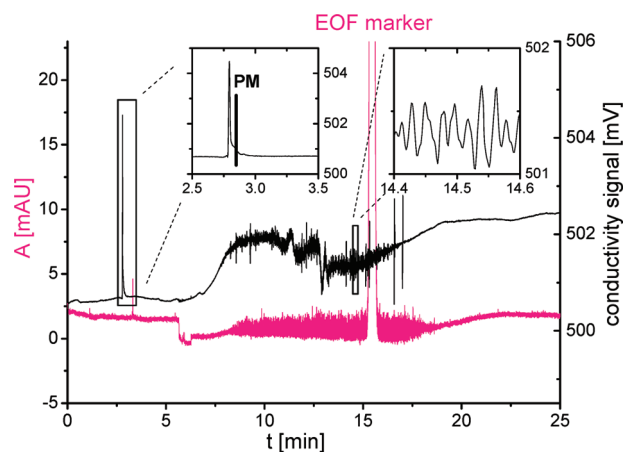


Figure 4. Electropherogram recorded by UV absorbance at 191 nm for oscillation system D: 2.152 mM acetic acid, 1.906 mM citric acid, 6.760 mM Na^+ . Black and pink curves are the records of the conductivity detector and UV detector (191 nm), respectively. The vertical black line denoted by PM shows the calculated position corresponding to the real part of the complex system eigenmobility.

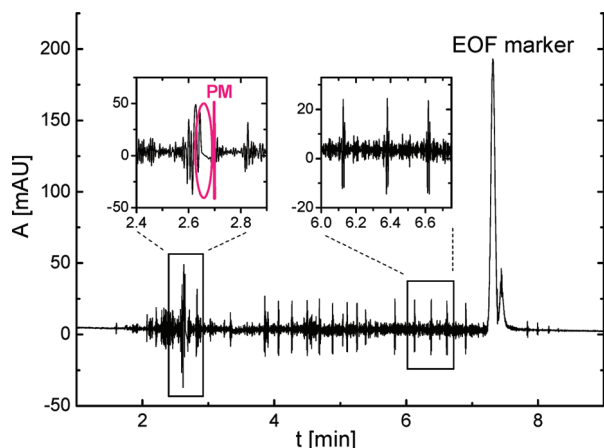


Figure 5. Electropherogram recorded by UV absorbance at 214 nm for oscillation system E: 3.995 mM maleic acid, 1.232 mM phthalic acid, 7.533 mM Na^+ . For details, see the text and Figure 1.

Obviously, complex system eigenmobilities can appear not only for a single solution composition but also for a certain concentration range of all constituents. These concentrations form a subspace in three-dimensional space, with the coordinates being the concentrations of the three constituents. As such a subspace is difficult to depict, a two-dimensional plot is shown in Figure 1c, in which the concentrations of two constituents form the two perpendicular coordinates, whereas the concentration of the third is fixed. The horizontal axis shows the concentration of phosphoric acid from 3 to 25 mM and the vertical axis of Na^+ ions from 10 to 60 mM; GMP concentration is fixed at 5.000 mM. The yellow-violet area comprises compositions of the mixture exhibiting complex eigenmobilities, and the various shades of gray are compositions with real eigenmobilities. The composition of the electrolyte inspected experimentally (5.000 mM GMP, 5.000 mM phosphoric acid, and 14.200 mM Na^+) is a green point in the yellow-violet area. According to PeakMaster, an additional area with systems composed of 5.000 mM GMP and phosphoric acid plus Na^+ should have complex eigenmobilities. This is in the range of higher concentrations of phosphoric acid and Na^+ and is shown as a second elliptic violet area in Figure 1c. However, this system was not experimentally tested.

4.2. Other Ternary Oscillation Systems. In the course of our investigations, we discovered a number of electrolyte systems with complex system eigenmobilities, which should show oscillating behavior analogous to system A, but have some distinctive features. The compositions of some are also given in Table 1. The systems were prepared from the chemicals as listed in Table 2, and the data used for the calculations (which are implicit in the built-in database of PeakMaster) are listed in Table 3. Like system A, the systems are composed of three constituents, of which at least one has a valence higher than one, so all the systems have three eigenmobilities—one being close to zero and the other two forming a complex conjugate pair. In some cases, the composition of the systems had to be slightly modified in the experiments to produce oscillations. Table 1 gives both the composition calculated by PeakMaster and the composition used in the experiment, and Table 2 summarizes the experiment results. For the small deviation between the theoretical and experimental compositions in systems B, C, D, and E, we consider two sources of error to be contributing. (i) The limited accuracy of the input data—ionic mobilities and pK_a values—of the compounds. (ii) The correction for ionic strength according to Onsager–Fuoss²¹ used in PeakMaster may not yield accurate mobilities, especially for ions with charge higher than one in absolute value.

In agreement with the theoretical prediction, all systems having complex eigenmobilities listed in Table 2 indeed exhibited oscillations in the capillary electrophoresis instrument. After some initial time, the originally uniform concentrations of the constituents in the capillary started forming periodic patterns of various shapes, in some cases chaotic. The spatial period of oscillations was about 1–4 mm, depending on the system. To form an initial disturbance in the solution, we injected a short plug of the electrolyte—similarly as in experiments with system A—with the same constituents but with 10% lower concentration plus 5 mM thiourea, which served as the EOF marker.

System B: Maleic Acid/Citric Acid/ Na^+ . According to the results obtained by PeakMaster (see Table 2) the system composed of 4.000 mM maleic acid, 1.136 citric acid, and 7.129 mM Na^+ ions should show oscillations as the complex pair of eigenmobilities is $(-44.87 \pm 0.48i) \times 10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$. To obtain this oscillation, however, we had to modify the composition slightly and adjusted the Na^+ concentration to 7.450 mM. Oscillation starts at about 1 min (Figure 2), but unlike the system GMP/phosphoric acid/ Na^+ oscillation stops at about 15 min. The possible reason for this effect will be discussed below.

System C: Chromic Acid/Phthalic Acid/ Cs^+ . Contrary to system A, it was rather difficult to produce oscillations with this system because CrO_4^{2-} ions are in equilibrium with $\text{Cr}_2\text{O}_7^{2-}$ ions, depending on concentration and pH. Further, ionic mobilities of both chromate and dichromate ions given in the literature are rather uncertain. However, the system composed of 4.414 mM chromic acid, 2.734 mM phthalic acid, and 9.662 mM Cs^+ ions exhibited oscillations (prediction by PeakMaster was for 3.414 mM chromic acid, 2.734 mM phthalic acid, and 9.662 mM Cs^+). Oscillations started at 7 min and stopped suddenly at 14 min (Figure 3). The real part of the complex eigenmobilities calculated by PeakMaster is $-51.08 \times 10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ (see Table 1), which should lead to the appearance of an injection irregularity in the electropherogram at 2.67 min under the given driving voltage, EOF, and capillary parameters. In this particular case, the system does not yet oscillate at this time, but the irregularity appears as a small zigzag feature at 3

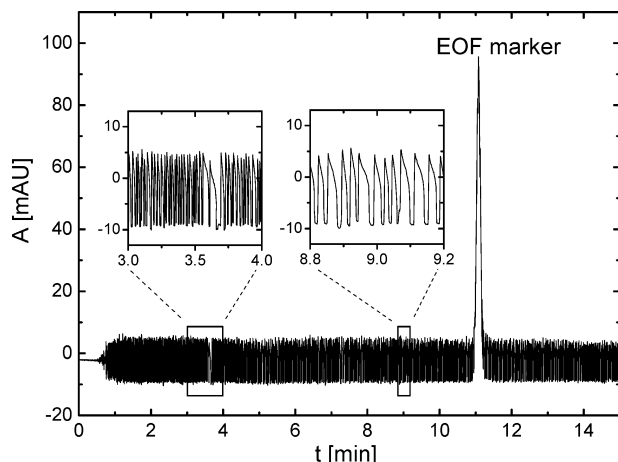


Figure 6. Electropherogram recorded by UV absorbance at 214 nm for the oscillation system composed of 0.935 mM GMP, 1.066 mM phosphoric acid, and 2.805 mM Na⁺. Amplitude of oscillations is about 15 mAU. For details, see the text and Figure 1.

min denoted by a pink ellipse in the inlay. Still, the agreement of the predicted (PM) and experimental (ellipse) position is very good.

System D: Acetic Acid/Citric Acid/Na⁺. This oscillation system is composed of very common chemicals. To obtain the oscillations—based on the complex eigenmobility pair of $(-41.86 \pm 0.56i) \times 10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ —we modified the concentration of sodium ions. The experimentally oscillating system is composed of 2.152 mM acetic acid, 1.906 mM citric

acid, and 6.760 mM Na⁺. None of the constituents significantly absorb UV light, so a rather short wavelength (191 nm) was used in the UV detector, which led to a somewhat noisy signal. For this reason, we also used the CCD in series.¹⁸ Unfortunately, the axial spatial period of the oscillation is around 1 mm in this system, and since the width of the detection window of the CCD is about 2 mm the signal is diminished due to the low CCD axial resolution. Figure 4 shows the records of both detectors, which are located at the capillary 6.5 cm apart from each other. Obviously, the neutral UV marker is clearly visible only in the UV record. The real part of the complex eigenmobilities calculated by PeakMaster is $-41.86 \times 10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ (Table 1); the corresponding injection irregularity is recorded at 2.85 min with the CCD, marked by the black vertical line (PM) in the inlay of Figure 4. It can be seen that the experimental irregularity appears as a sharp peak very close to the calculated position.

System E: Maleic Acid/Phthalic Acid/Na⁺. The system composed of 3.995 mM maleic acid, 1.232 mM phthalic acid, and 7.533 mM Na⁺ (which slightly deviates from the predicted 7.433 mM) also gives a pattern of oscillations (Figure 5). This system differs from the previous in that the constant amplitude of waves is interrupted at almost regular intervals by bursts of undulations with much higher amplitude.

4.3. Amplitude of Oscillations. We demonstrated above that the amplitude of oscillations is a parameter easily obtained from experiments. In most cases, we found that the amplitude of the oscillations remained almost constant; however, in some cases, the oscillations ceased after some time. We explain this stop by a gradual change in the composition of the electrolyte due

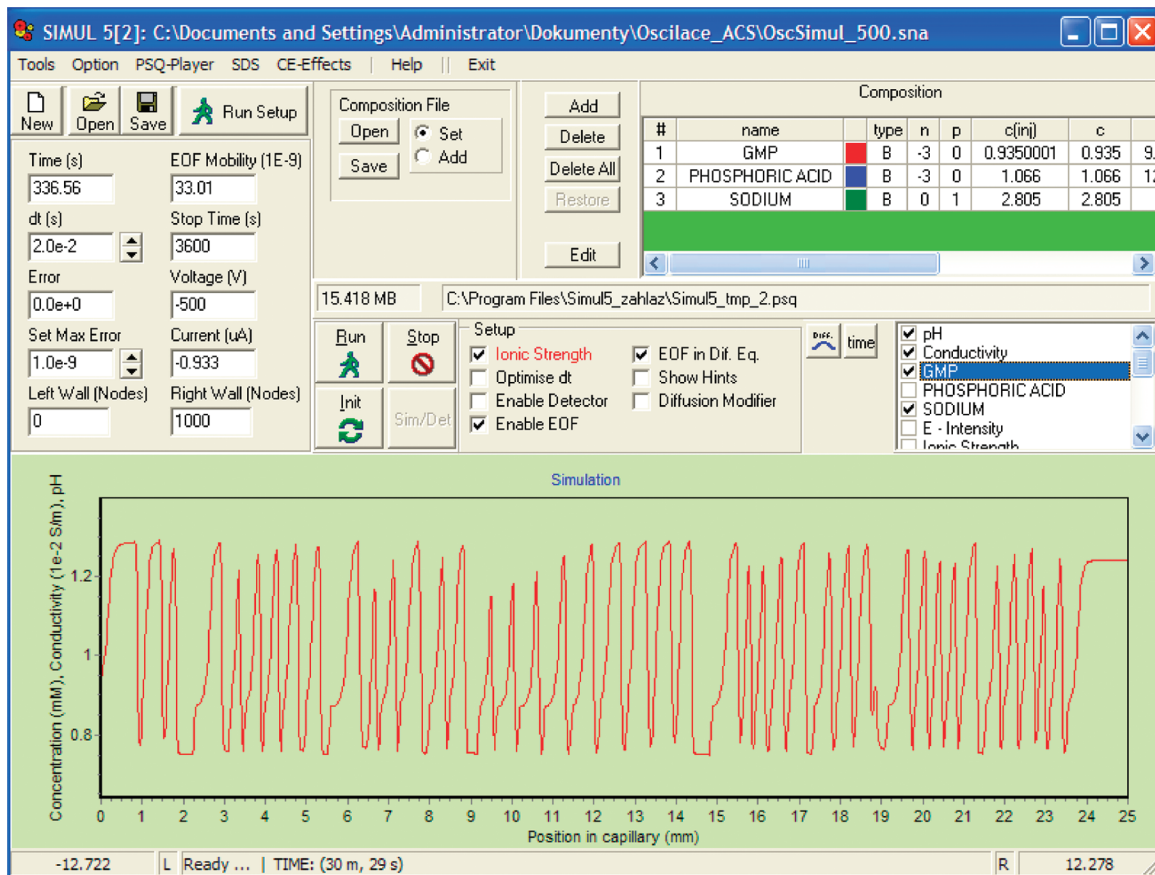


Figure 7. Computation window of Simul with the developed limiting oscillations for the system composed of 0.935 mM GMP, 1.066 mM phosphoric acid, and 2.805 mM Na⁺, showing the axial distribution of the GMP concentration in a 25 mm segment of the capillary. Amplitude of oscillations is about 0.55 mM.

to electrolysis at the electrodes in the vessels. The electrolyte altered in this way is transported through the capillary by the EOF, and the composition gradually falls outside the oscillation range.

An explanation of the phenomenon that there is almost constant amplitude most of the time is a complex task. The linear theory of electromigration merely indicates that the system is potentially unstable and capable of oscillation when the eigenmobility is complex. The direct periodic solution of the linearized equation, eq 4, which we will present elsewhere, simply shows that the amplitude increases to infinity with increasing time, which obviously cannot happen in reality. Note that it was a prerequisite for the linear model that the disturbances in concentrations were regarded as being small. This is clearly not fulfilled for oscillations with high amplitude. In these cases, a complete nonlinear model of electromigration must be employed for a correct prediction of the amplitude of oscillations. Such models have been described elsewhere by us and several other authors^{22–26} and can only be solved numerically. We have developed the freely available software Simul,²⁷ which numerically solves the nonlinear dynamic model of electromigration, so it should correctly account for the phenomena taking place in oscillating electrolytes. The outputs of the simulation by Simul are spatial distributions of the concentrations of all constituents over time. For easy comparison of the simulation with experiments, it is therefore favorable to select a system which contains only one constituent giving a response in the detector. A system composed, e.g., of 0.935 mM GMP, 1.066 mM phosphoric acid, and 2.805 mM Na⁺ (analogous to system A) can fulfill this requirement, as at 214 nm (the wavelength chosen for detection) the only absorbing constituent is GMP. We experimentally determined a linear calibration line relating the concentration c of GMP (in mM) and the absorbance signal A of the detector (in mAU), with the resulting equation $A = 30.785c + 0.164$. The experimental electropherogram, Figure 6, shows the oscillation in the absorbance signal, the amplitude of which is about $A = 15$ mAU. This corresponds to the amplitude for the GMP concentration $c = 0.48$ mM. Simulation of the electromigration behavior of this system by Simul software nicely illustrates that the amplitude of oscillations increases exponentially at the beginning but later slows and eventually levels off to a constant value. This limiting situation is shown in Figure 7, depicting the simulated axial distribution of GMP in a 25 mm long part of the capillary. The amplitude of the limited GMP oscillation is about 0.55 mM, which is in very good agreement with the experimental value of 0.48 mM.

5. Conclusions

Electromigration oscillations presented here demonstrate an interplay between theory and practice: the oscillations could only be explained and experimentally demonstrated when the theory of electromigration predicted their existence. We confirmed that the existence of complex system eigenmobilities is the unequivocal criterion for the instability of the electrolyte system and its ability to behave chaotically or oscillate when conducting an electric current. Several ternary oscillation electrolyte systems were found when searching concentration regions where complex eigenmobilities occur. All these oscillation systems are formed from a base and two acids, of which at least one has a higher valence than one in absolute value. The systems have three system eigenmobilities: one is real and close to zero, and

the two other form the complex conjugate pair, the real part of which is far from zero. The oscillations start at a certain period of time after switching on the driving electric current. The originally uniform concentration attains an almost periodic pattern in space, with a spatial period in the range of 1–4 mm and almost constant amplitude. The periodic pattern electrophoretically moves in the electric field with mobility which is equal to the real part of the complex eigenmobility pair. We believe that oscillating electrolyte solutions sometimes appear in capillary electrophoresis practice but that their oscillating behavior is misinterpreted as electric or electronic malfunctions of the analytical system. It can be supposed that other oscillating electromigration systems exist, e.g., composed of one acid and two or more bases or composed of more than three constituents.

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