



Conditions for nonlinear kinetic effects in multispecies ion exchange (MIE)

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Abstract

The kinetics of MIE is theoretically analyzed to reveal the occurrence of macroscopic electric fields. An experimental technique to detect these fields is proposed. Self-oscillations in MIE systems are obtained. Relations between the amount of a microcomponent introduced into a MIE system and the reciprocal electric signal are determined. Numerous examples presented attest that the process of transient multispecies ion exchange generates a macroscopic electric field. This new phenomenon could be applied to ion analysis. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The nonlinear kinetic effects in MIE are associated with violations in the monotone approach of some ionic components to an equilibrium under constant interphase boundary conditions. Such an effect was first theoretically predicted by Hwang and Helfferich in 1987 [1]. A further development of the MIE theory and the first direct experimental observation of the effects have been made in our papers [2,3]. In these works, conditions necessary for observing the nonlinear effects in MIE kinetics were analyzed and an explanation of the effects was proposed. The origin of the effects consists in the occurrence of a macroscopic electric field in an ion-exchanger grain. This field can violate the monotone particle diffusion of counterions, that is the principal distinction of the MIE kinetics from the conventional two-component ion-exchange kinetics. A mathematical model developed for the phenomenon allows us to

conclude that for the occurrence of the effect it is necessary that the least mobile counterion would move in the direction of moving that more mobile ion whose kinetic curve passes through the maximum.

2. Theory

The so-called macroscopic model has been proposed as an asymptotic approach describing MIE-processes [2]. It implies the kinetic equation for a MIE-process:

$$\frac{da_i}{dt} = \frac{2\pi^2 D_i}{3d^2} a_{0i} - a_i \left(+ z_i \frac{\sum D_j z_j (a_{0j} - a_j)}{\sum D_j z_j^2 a_j} \right) \quad 1)$$

where a_{0i} and a_i are the equilibrium and current concentrations of the i th ion in an ion ex-

changer, z_i and D_i are the charge (in electron-charge units) and the ion diffusivity; t is the time, and d is the diameter of a spherical grain of the ion exchanger. The comparison of the calculation results based on the Eq. (1) of the macroscopic model with the results for the same example based on the locally-determined model by Hwang and Helfferich was satisfactory (Ref. [2], Fig. 1). A series of calculations using Eq. (1) allowed us to determine conditions for obtaining the kinetic effects.

The experimental procedure well-known as the “shallow-bed” method was used for studying MIE kinetics on a Dowex-50 analogue in Russia – a KU-2 cation-exchanger. The results of those experiments for various combinations of ionic components were shown on the plots (Ref. [2], Fig. 2). Those experiments had first demonstrated the effects of MIE kinetics predicted on the basis of the macroscopic model.

The main conclusion following from the macroscopic model was the above-mentioned hypothesis of the macroscopic electric field

(MEF). Our further works have been devoted to verifying the MEF hypothesis, as well as to detecting and applying the effects of electric field [4].

Calculations of the time derivative of the potential using the macroscopic model:

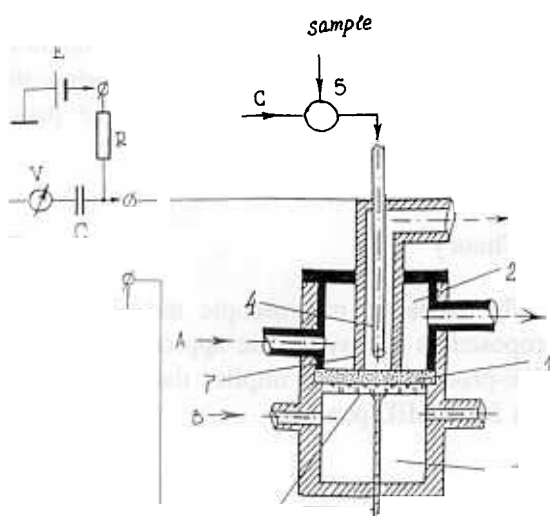
$$\phi_0 - \phi = - \frac{2RT}{F} \frac{\sum D_j z_j (a_{0j} - a_j)}{\sum D_j z_j^2 a_j}$$

(T is the temperature, R and F are the gas and Faraday constants) yield a Gaussian like curve with the maximum fairly close to the maximum of the kinetic curve. This implies that, in the neighborhood of the maximum of the kinetic curve, the kinetic equation can be written as:

$$\phi - \phi_0 \equiv \phi_{\text{MIE}} \approx \frac{RT}{F} \frac{(a_{0x} - a_x)}{z_x a_x} = - \frac{RT}{F z_x} \Delta_x$$

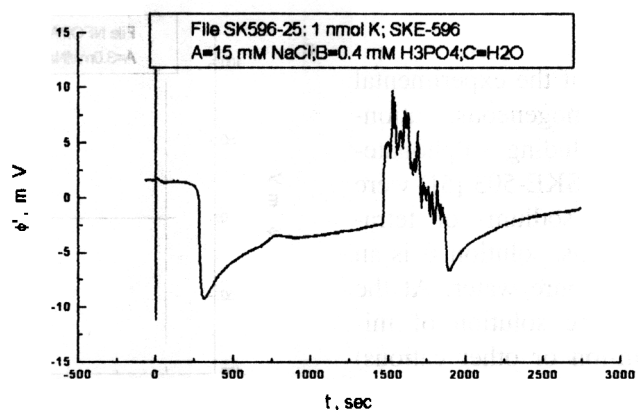
Thus, we can conclude that the relative overshoot (Δ_x) of the maximum sorption uptake in comparison to the equilibrium sorption uptake for the most mobile ion “ x ” is the main reason why the electric potential (ϕ) deviates from the equilibrium value (ϕ_0).

The second conclusion evident from the theory is that the magnitude of the electric field substantially decreases with penetrating co-ions into the ion-exchanger. This is due to the free distribution of the co-ions within the electric field induced as a result of the motion of counterions. Actually, the Donnan effect, that is, the boundary electrostatic barrier of the same polarity as the co-ions, prevents their penetration into the ion-exchanger phase. A combination of the macroscopic electric field arising in the ion-exchange kinetic process and the Donnan electrostatic potential can lead to a controllable breakthrough of the co-ions and, in particular, can generate a self-oscillation process. The experimental possibilities for observation and amplification of the MEF are considered below.

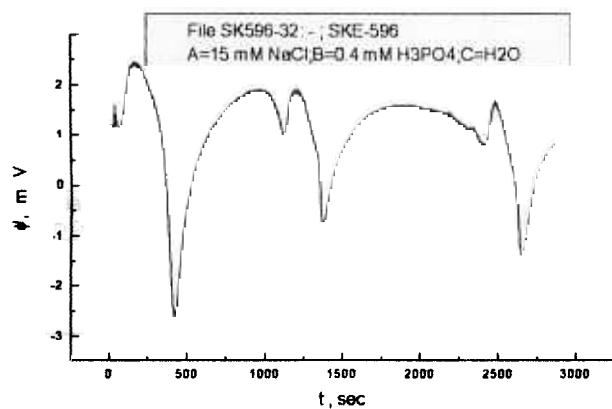


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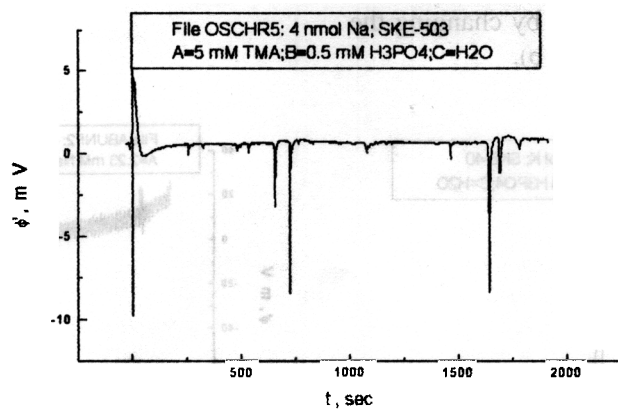
Fig. 1. Schematic of three-component ion-exchange system and electric circuit for measurement: ion-exchange membrane (1); supporting cells (2), (3); pure cell (4); injector (5); grid electrode (6); orificed electrode (7); C is condenser; V is voltmeter; R is resistor; E is external potential. A, B, C are solutions.



(a)



(b)



(c)

Fig. 2. Effect of self-oscillations under large amount of third component injected.

3. Experimental

Fig. 1 shows a schematic of the experimental device. Various types of homogeneous, cation-exchanging membranes (including sulphonate-containing aryl-polyamide – SKE-503 [5]) were used. Solution A contains sodium- or tetramethylammonium (TMA)-ions, solution B is an acid, and solution C is the pure water. At the onset of the experiment, the solution of microcomponent (potassium-ion or other cations) was injected in short-time into the solution C flow. The electric circuit is aimed to measure the potential agility and to control the membrane potential.

4. Results and discussion

Numerous examples demonstrate the electric effects of MIE kinetics. Fig. 2a–c shows the self-oscillation effect. The experimental conditions are indicated in the figure legend which gives: file name; amount of the microcomponent injected; type of the membrane; concentrations and nature of solutions A, B and C.

Figs. 3 and 4 exhibit the effects of frustration and reversible disturbance of the basic state. Also we can see the capability of the system to return itself into the basic state by changing the external potential (Fig. 5a and b).

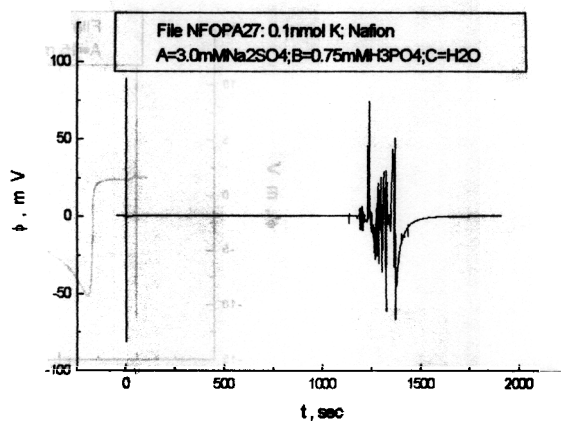


Fig. 4. Effect of reversible disturbance of the basic state.

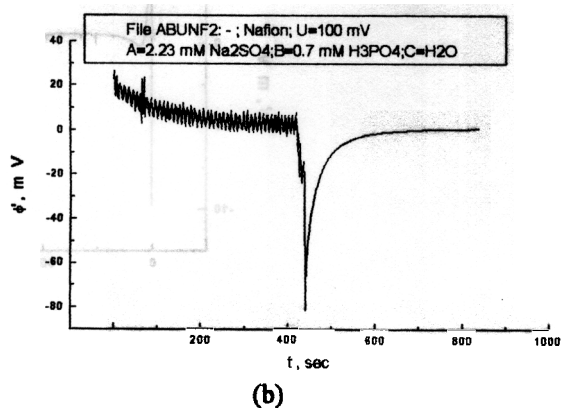
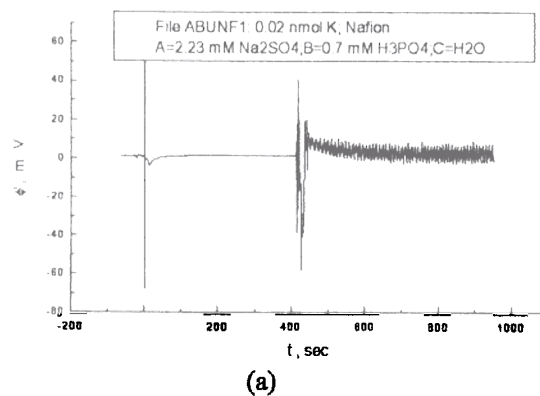


Fig. 5. Capability of the system to return to the basic state by changing the external potential.

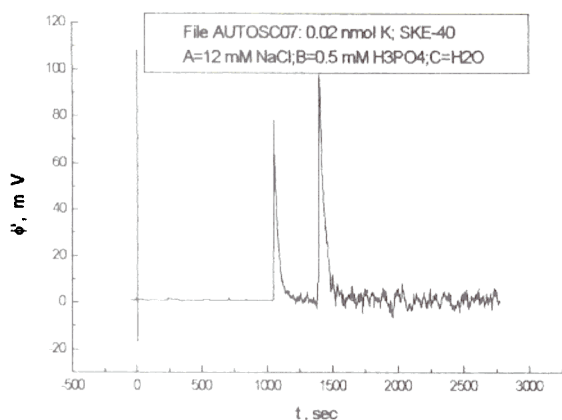


Fig. 3. Effect of frustration of the basic state.

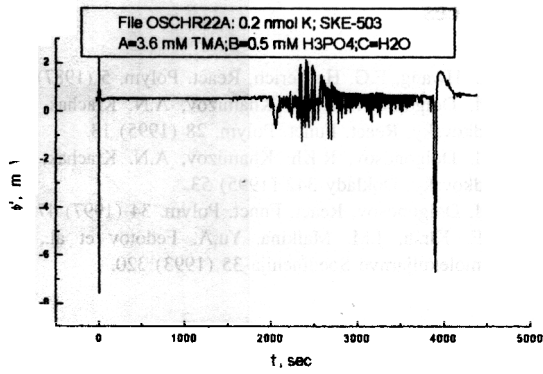


Fig. 6. Three stages of the effect of reversible disturbance of the basic state: frustration (approx. 2000–2700 s); self-oscillation (2700–3700 s); a peak before stabilization (3900 s).

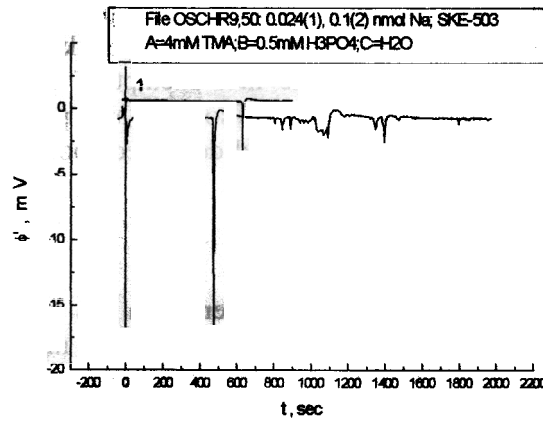
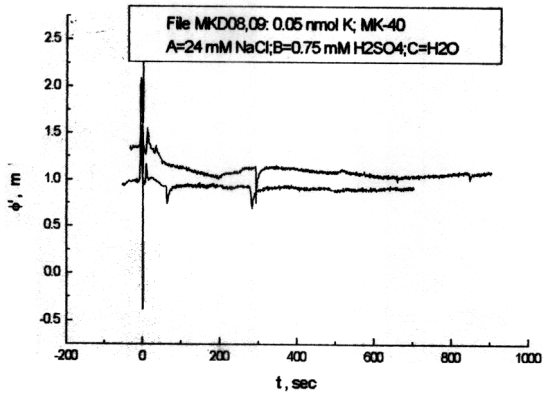
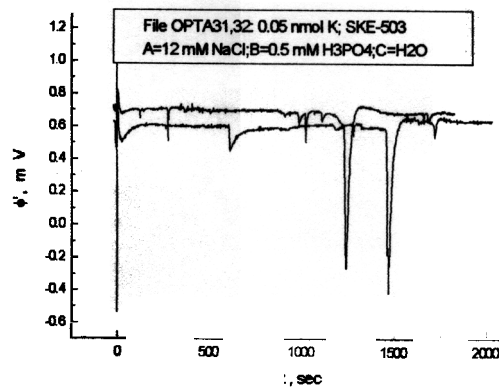


Fig. 8. Linearity of the effect for sodium in the system with TMA solution.



(a)



(b)

Fig. 7. Reproducibility and sensitivity of the effect for a very low amount of potassium.

Fig. 6 shows three stages of the reversible disturbance of the basic state:

- frustration;
- self-oscillation;
- burst before stabilization.

Fig. 7a and b demonstrates low reproducibility and high sensitivity of the effects under study. Fig. 8 illustrates the linearity of the response to the amount of sodium ion.

Fig. 9 shows the results of three consecutive experiments, where (1) sodium, (2) potassium

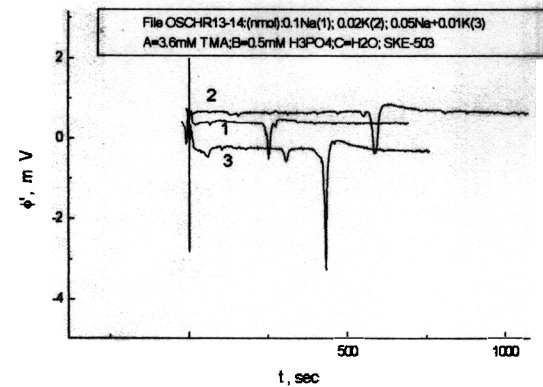


Fig. 9. Effect of sodium-potassium separation. (1) curve for sodium ion individual solution; (2) curve for potassium ion individual solution; (3) curve for 1/1 mixture of the solutions of sodium and potassium ions.

and (3) a 1:1 mixture of sodium and potassium were injected. TMA and protons were taken as macro-ions. This is the first attempt of chromatographic separation of sodium and potassium ions using the method described above.

5. Conclusion

A series of examples presented in this paper suggests that the process of transient multi-species ion exchange generates a macroscopic electric field. This phenomenon could be applied to ion analysis.

Acknowledgements

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