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GENERATION OF ELECTRICITY IN LOW-CONDUCTIVITY LIQUIDS AS A DETECTION PRINCIPLE IN LIQUID CHROMATOGRAPHY

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SUMMARY

A detection principle is described that is based on the measurement of streaming current. Relationships are presented that describe the generation of electricity in low-conductivity liquids during their flow through a capillary or a porous bed. By virtue of the theory of an electrical double layer, the dependence of the magnitude of the electrical current transported by the liquid on the composition of the mobile phase and the nature of the phase interface is derived. The response, *i.e.*, the electrical current, has the character of a mass-sensitive response. The detection principle is non-selective and non-destructive.

INTRODUCTION

Despite the rapid development of instrumentation associated with liquid chromatography in recent years, the detector still remains a limiting factor in the utilization of this method for trace analysis. In most instances the sensitivity of liquid chromatographic detectors still does not reach that usual in gas chromatography. Mostly it is the stability of temperature, such as with refractive index detectors, or the requirement of a small volume of the measuring cell, such as with spectrophotometric detectors, that sets limits to further increases in the sensitivity of the present detectors.

We have employed a detection principle which is new in chromatography, *viz.*, the measurement of streaming currents in capillaries, orifices or adsorption beds[1]. After the phenomenon has been mastered theoretically with respect to the conditions of liquid chromatography, the principle may have some promise, especially owing to the great variability of the detection system (sorption surface–mobile phase), the technical simplicity of the design and electronics, and, in some instances, its high sensitivity and small contribution to zone spreading.

THEORETICAL

A streaming current is produced by the transport of a liquid that possesses an electrical charge. As a result of sorption equilibrium, a difference in the solute concentrations in the liquid phase and the interface boundary is established. At the same

time, there is also established a difference in the concentrations of charged particles, i.e., ions, so that the liquid and the interface boundary carry electrical charges of opposite signs. The distribution of charge about the interface boundary can be described by virtue of the theory of an electrical double layer, with regard to the special properties of liquids of low conductivity and low dielectric constant. According to contemporary concepts[2–6], the dependence of the potential in a liquid on the distance from the boundary can be characterized schematically as shown in Fig. 1. On contacting a surface that has a potential φ_s with a liquid, the adsorption of potential-determining ions or dissociation of surface groups leads to a change in the potential to a value φ_0. According to Stern's assumptions[7], on such a modified surface ions and molecules are adsorbed owing to non-electrostatic forces (forces of specific adsorption), to form an immobile part of the electrical double layer. This part of the double layer can be considered as a plane condenser of a thickness d constituting the distance between the surface and the plane of the centres of ions occurring closest to the surface. The potential of the outer side of this layer is usually denoted by φ_d. Behind this plane there is usually considered a share plane behind which the liquid is allowed to move relative to the interface boundary. The potential at this plane is usually called the ζ potential.
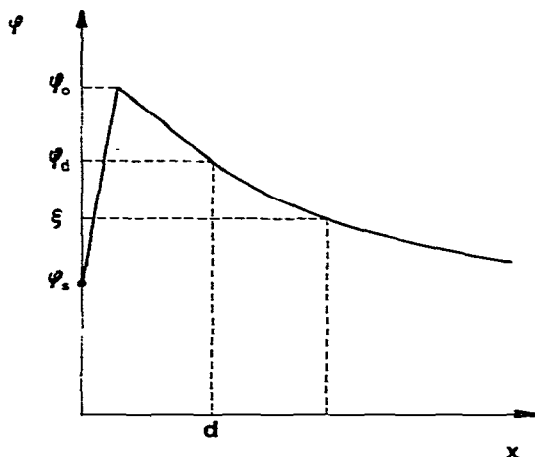

Fig. 1. Variation of potential with the distance from the surface. For symbols, see text.

The components of the liquid that occurs at a distance greater than d from the surface are influenced by electrostatic forces only. In dilute solutions of electrolytes, for calculating the distribution of potential or charge within this region of the liquid it is possible to apply the Gouy–Chapman theory of the diffusion part of electrical double layer[8,9]. The calculation is based on the equilibrium of diffusional and conductive charge fluxes between the boundary and the electrolyte. By solving the so-called linearized Poisson–Boltzman equation[10–12], we obtain the dependence of the course of the potential in a liquid on the distance from the plane surface in the form

$$\varphi = \varphi_d \exp(-\kappa x) \tag{1}$$

where $\kappa^{-1} = \sqrt{D\tau}$ is the so-called Debye–Hückel thickness of the ionic atmosphere, $\tau = \varepsilon/\varkappa$ is the relaxation time of the liquid, ε and $\varkappa$ being the permittivity and conductivity of the liquid and D being the diffusion coefficient of ions in the liquid. In the further treatment, we shall consider liquids with conductivities of $\varkappa < 10^{-9}\,\Omega^{-1}\!\cdot\!m^{-1}$ and relative permittivities of $\varepsilon_r < 5$. For these cases we have relaxation times $\tau > 10^{-2}$ sec and the parameter $\kappa^{-1} > 10\,\mu m$. As the plane at which we consider that $\varphi = \zeta$ is much closer than 10 μm to the surface, it is possible to introduce[13,14], with sufficient precision, $\zeta = \varphi_d$ and/or $\zeta = \varphi_0$ if specific adsorption does not occur in the system.

On solving the linearized Poisson–Boltzman equation for a liquid in a capillary of radius a, we obtain for the dependence of the potential on the distance r from the centre of the capillary[15–17]

$$\varphi = \varphi_d \cdot \frac{I_0\,(\kappa r)}{I_0\,(\kappa a)} \tag{2}$$

As it is possible to employ the Debye approximation[10,18] for the liquid considered, the relationship between the volume density of charge at the surface, q_s, and φ_d can be expressed as

$$q_s = \frac{2\,C_0 F^2}{RT} \cdot \varphi_d \tag{3}$$

On introducing a mean density of charge by[15,17]

$$q_{av} = \frac{2\pi \int_0^a q\,r\,dr}{\pi a^2} \tag{4}$$

the dependence of the distribution of charge in the cross-sectional plane of the capillary on the distance from the centre of the capillary can be expressed as[15]

$$q/q_{av} = \frac{\kappa a}{2} \cdot \frac{I_0\,(\kappa r)}{I_1\,(\kappa a)} \tag{5}$$

The dependence is illustrated in Fig. 2. It can be seen that for $\kappa a < 0.3$ the charge in the capillary can be considered, with a precision better than 5%, to be distributed uniformly over the cross-sectional plane[15,17].

The above derivation of the distribution of charge density in a liquid applies to the case of a liquid which does not move. For liquids that are moving, it is necessary to consider the charge transfer brought about by diffusion, conductivity, convection and surface reaction[16,19,20]. For a uni–univalent electrolyte, the cations and anions of which have the same diffusivities, the charge transfer is described by the equation

$$j = -D\,\nabla q - \varkappa\,\nabla\varphi + uq \tag{6}$$

where u is a local liquid velocity, $j = shq$ is a local surface reaction rate, s is the hydraulic surface of the adsorbent per unit volume (m^{-1}) and h is the mass-transfer
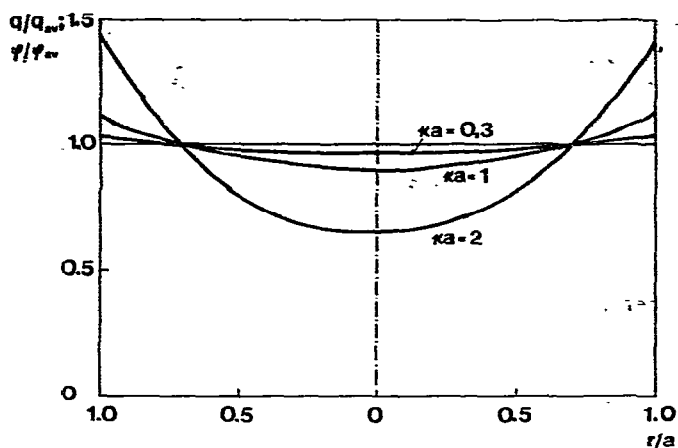
Fig. 2. Distribution of charge in low-conductivity liquids in tubes.

coefficient[21,22]. Provided that the charge is distributed uniformly over the cross-sectional area of the capillary of diameter a, and if, according to Gavis and co-workers[15,22],

$$D = \frac{\partial q}{\partial r}\bigg|_{y,\, r=a} = \frac{Fh}{n_+}(C_{-0} - C_{-s}) \tag{7}$$

where F is the Faraday constant, n_+ is the transfer number of the cation, C_{-0}, C_{-s} are concentrations of the anions in the liquid and at the surface, respectively, and y is the length of the capillary, by solving eqn. 6 we can express the dependence of the charge density q in the moving liquid on the coordinate y by the relationship[23,24]

$$q = \frac{sh\tau}{1 + sh\tau}\, 2F(C_{-0} - C_{-s}) \left[1 - \exp - (1 + sh\tau)\frac{y}{\bar{u}\tau}\right] \tag{8}$$

The boundary condition quoted in eqn. 7 and the solution of eqn. 8 involve the assumption of preferential adsorption of negative ions at the interface boundary. Further, in deriving eqn. 8, it has been assumed that the entering liquid is not charged and that the transfer numbers of the cations and anions are 0.5. Eqn. 8 describes the dependence of the charge density in the liquid on the length of the capillary, the relaxation time, the rate of charge transfer through the boundary and phase equilibrium of the ions. In the equation, the local velocity, u, can be replaced with an average linear velocity, $\bar{u}$, as a uniform distribution of charge over the capillary cross-section has been considered[15,22]. In deriving this equation, the effect of changes of charge density on the conductivity of the liquid has also been neglected. As will be shown later, for particular values of the individual quantities eqn. 8 can be simplified.

Eqn. 8 indicates the dependence of the charge density on the concentration of the ions of the component considered in the solution. The dependence of the charge density on the analytical concentration of a component i, c_i, can be derived from the dependence of the charge density on the potential of the phase interface. According

to the Debye approximation[3], and if the charge is distributed uniformly over the capillary cross-section, q_{av} can be expressed as

$$q_{av} = \frac{2C_0 F^2}{RT} \cdot \varphi_d \tag{9}$$

where $C_0 = C_{-0} = C_{+0}$ is the concentration of the ions in the bulk liquid ($\varphi = 0$).

Denoting the potential of the surface covered by a monolayer of component i and the potential of the non-covered surface by φ_i and φ_0, respectively, the dependence of φ_d on the coverage θ_i can be described by

$$\varphi_d = (\varphi_i - \varphi_0)\,\theta_i + \varphi_0 \tag{10}$$

As a change in the concentration c_i of the components also brings about a change in the permittivity of the liquid, which influences the degree of dissociation of ionizable components of the solution[25,26], the concentration C_0 is a function of c_i, and the coverage θ_i is also a function of c_i. Therefore, the dependence of the average charge density, q_{av}, on the concentration of the component, c_i, can be written in the differential form as

$$dq = \frac{2\,F^2}{RT}\,(\varphi_i - \varphi_0)\left(\theta_i \cdot \frac{\partial C_0}{\partial c_i} + C_0 \cdot \frac{\partial \theta_i}{\partial c_i}\right) dc_i \tag{11}$$

The dependence of the electrical conductivity of the liquid on the change of its permitivity has an exponential form[25–27], and as the relationship

$$\varkappa = \frac{2\,C_0\,F^2\,D}{RT} \tag{12}$$

holds for a uni–univalent electrolyte with the cations and anions having the same diffusivity, we can derive

$$\partial C_0 / \partial c_i = C_0 A \tag{13}$$

where A is a constant characteristic of the solvent and solute. Further, for the linear region of the adsorption isotherm we have

$$\frac{\partial \theta_i}{\partial c_i} = K_{di}/c_{si}^0 \tag{14}$$

where $K_{d\,i} = c_{s\,i}/c_i$ is the distribution constant and c_{si}^0 is the maximum surface concentration of component i. In eqn. 11, for $K_{d\,i}/c_{s\,i} \geqslant A$, we shall have $\theta_i \cdot \partial C_0/\partial c_i \ll C_0 \cdot \partial \theta_i/\partial c_i$ and, employing eqns. 12 and 11, we can write the dependence of the average charge on the concentration of the component as

$$\frac{d\,q_{av}}{d\,c_i} = \frac{\varkappa}{D} \cdot \frac{\varphi_i - \varphi_0}{c_{si}^0} \cdot K_{di} \tag{15}$$

When evaluating the response of the detection system with respect to its dependence on the composition of the mobile phase, solute concentration and chemical nature of the surface, it is necessary to start from eqns. 8 and 15.

RESULTS AND DISCUSSION

If the charge is distributed uniformly in the liquid, which has been assumed in deriving eqns. 8 and 15, then the streaming current, I_{str}, can be expressed as the product of charge density, q, and volumetric liquid flow rate, F_m:

$$I_{str} = dQ/dt = F_m q \tag{16}$$

where Q is the overall charge in the volume of liquid having flowed through. It is evident that the response of this detection system in liquid chromatography is the electrical current, I_{str} (A), and the peak area is equal to the electrical charge, Q (A·sec). The detection system is of mass-sensitivity character. Further, this detection system does not require any converter of the analytical property to the response. The streaming current can be measured directly with an electrometric amplifier and/or, in some instances, directly with a recording millivoltmeter. The properties of the electrometric amplifier are determined by the requirement that the imput resistance of the amplifier should be sufficiently small compared with the resistance of the liquid within the space in which the measurement is carried out; however, the sensitivity of the arrangement is proportional to the magnitude of the input resistance. Depending on the mobile phase system employed, the input resistance of the electrometric amplifier varies within the range 10^6–10^{10} Ω.

The properties of the detection system were proved experimentally by employing a laboratory-made liquid chromatograph (an MC-300 pump, Mikrotechna, Prague, Czechoslovakia, and/or an DMP 1515 pump, Orlita, Giessen, G.F.R.; pressure-shock dampers according to Locke[28]; a septum inlet port; an HP 305 syringe, Hamilton, Reno Nev., U.S.A.; a 250 × 2 mm I.D. column; and silica gel, 30–40 μm, Lachema, Brno, Czechoslovakia).

A schematic diagram of the electrokinetic detector with a capillary as the detection element is shown in Fig. 3. In Fig. 3a, the streaming current is generated in a bundle of about 200 glass capillaries (1) with inner diameters of about 20 μm, the outer diameter of the bundle being about 1 mm. Bundles of capillaries of length 20 and 100 mm were tried. The bundle of capillaries was connected to the column via a PTFE seal (2) and the liquid was drained off by a PTFE capillary (3). The streaming current was picked up from the capillary bundle by means of a copper wire (0.2 mm in diameter) wound over the full length of the bundle and led via a connector (4) to a 33B-2 Vibron electrometer (Electronic Instruments, Surrey, Great Britain) (5). Input resistances of 10^9–10^{10} Ω were employed. Lower alcohols were separated using n-hexane–isopropanol (95:5) as the mobile phase, and the effect of the length of the capillaries on the magnitude of the streaming current, depending on the mobile phase flow-rate, was studied.

On analyzing the quantities in eqn. 8, it can be shown that with the geometry of the capillaries and the mobile phase employed, the equation can be simplified to
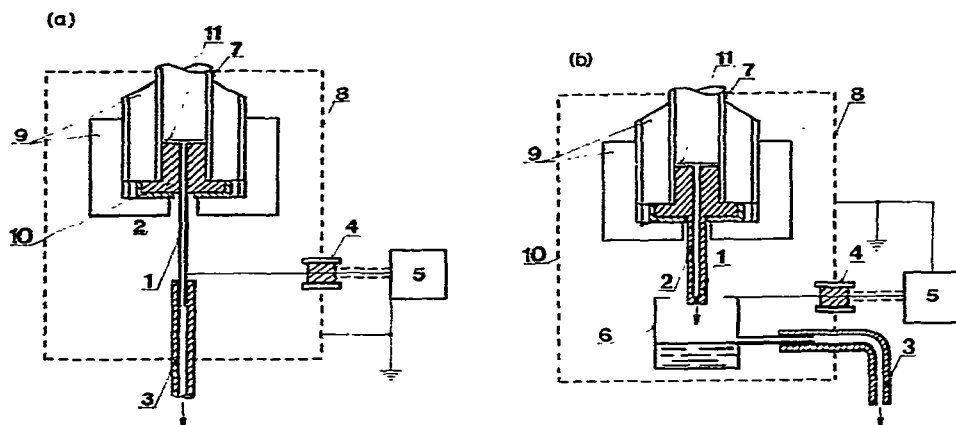
Fig. 3. (a) Schematic representation of the electrokinetic detector with a bundle of about 200 capillaries (1) of about 10 cm in length and 20 μm in diameter, made by drawing a glass tube packed with glass capillaries. 2 = PTFE seal of the column; 3 = PTFE capillary for draining off the mobile phase; 4 = connector; 5 = electrometric amplifier; 7 = chromatographic column; 8 = earthed shielding; 9 = screw closure of the column; 10 = metal washer to the column closure; 11 = filter-paper. (b) Schematic representation of the electrokinetic detector with a PTFE jet (1) of I.D. 20 μm and length 1 mm. 6 = Effluent collector; other components as in (a).

obtain the form derived by Gavis and Koszman[15]. Because $s = 2/a$ and $h = D/\delta$, $s\,h\tau \ll 1$ for the system employed and eqn. 8 assumes the form

$$q = s\,h\,\tau\,2F(C_{-0} - C_{-s})\,[1 - \exp - y/\bar{u}\tau] \tag{8a}$$

If further $y \gg \bar{u}\tau$, it is possible to neglect the exponential term in eqn. 8a. The results of the measurements are shown in Fig. 4. In compliance with the above-mentioned
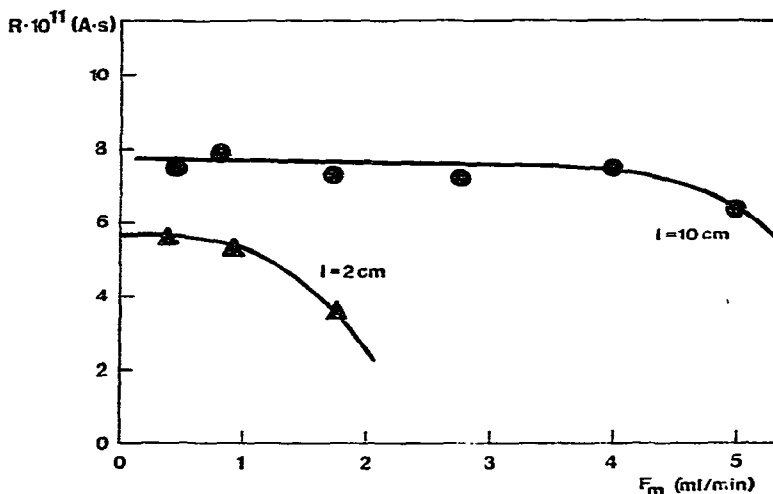

Fig. 4. Dependence of response (R) of the electrokinetic detector shown in Fig. 3a on the volumetric flow-rate (F_m) of mobile phase and the length (l) of the glass capillary bundle. Mobile phase, n-heptane–isopropanol (95:5); 1-μl sample of ethanol. Vibron M 33B-2 electrometric amplifier with a 10^9 input resistance; each point represent an average value of three measurements.

assumption, it can be seen that the interval within which the response is independent of the flow-rate of the mobile phase increases with increasing length of the capillary. Under these circumstances, the response $Q = \int I_{str}\, dt = R$ is independent of the flow-rate of the mobile phase and has the character of a mass-sensitive response.

If a condition opposite to that quoted above applies, *i.e.*, $y \ll \bar{u}\tau$, it is possible to obtain, by using the first two terms of the expansion of the exponential term[15] in eqn. 8a, an expression for the case of a very short capillary (orifice):

$$q = \frac{y\,s\,h}{\bar{u}} \cdot 2F\,(C_{-0} - C_{-s}) \tag{8b}$$

Under these conditions, the response has a concentration-sensitive character.

An arrangement with a very short capillary is shown in Fig. 3b. A capillary (1) of about 20 μm in diameter and 1 mm in length was a part of the PTFE seal (2). In contrast to the case shown in Fig. 3a, the streaming current is picked up from a stainless-steel holder of mobile phase (6), which is electrically insulated both from the jet and from the earthed shield. The liquid is drained off via a PTFE capillary (3). The holder (6) is connected, via a connector (4), to the electrometric amplifier (5). In separating the isomers of nitroaniline, n-hexane–isopropanol (85:15) was employed as the mobile phase. The dynamic linear range of response towards m-nitroaniline was about 10^3; the result is shown in Fig. 5.

As it has been derived[17,29], eqn. 16 holds for any shape of capillary cross-section. Hence it is possible to use also a porous bed for generating the streaming current and to study the dependence of the response on the chemical nature of the surface and/or on the distribution constant according to eqn. 15. When applying eqn. 8 to the flow through a porous bed formed by beads of about 10 μm in diameter, it is possible to assume that, for velocities up to about 10 cm/sec, the following conditions are fulfilled: $sh\tau \gg 1$ and $hsy/\bar{u} \gg 1$ for $y > 1$ mm. At the same time, in order to be able to neglect the effect of axial diffusion, it is necessary that the condition $\bar{u} \gg 30\, D/y$ also be fulfilled[30]. The magnitude of the hydraulic surface[31] is a function of the particle diameter, $s = 6/d_p$, and the mass-transfer coefficient, h, in a region for which $0.04 < Re < 30$, can be expressed by the relation[31] $h = 5.4\,(D/d_p)$ $Re^{1/3}\,Sc^{1/4}$, for instance. Hence, the exponential term in eqn. 8 can be neglected and, as we consider the ion concentrations C_+ and C_- to be distributed symmetrically about the concentration C_0, we can assume that

$$q = q_s = q_{av} \tag{17}$$

(*cf*. Fig. 2 for the condition $\kappa a \ll 1$).

From eqns. 15, 16 and 17, we obtain for the sensitivity of the detection system

$$\frac{d\,I_{str}}{d\,c_i} = \frac{\varkappa}{D} \cdot \frac{(\varphi_i - \varphi_0)}{c_{si}^0} \cdot K_d\,F_m \tag{18}$$

For a chosen chromatographic system, the right-hand side of eqn. 18 is constant. The mobile phase is characterized by $F_m\varkappa/D$ and the stationary phase and solute by $(\varphi_i - \varphi_0)K_d/c_{si}^0$.
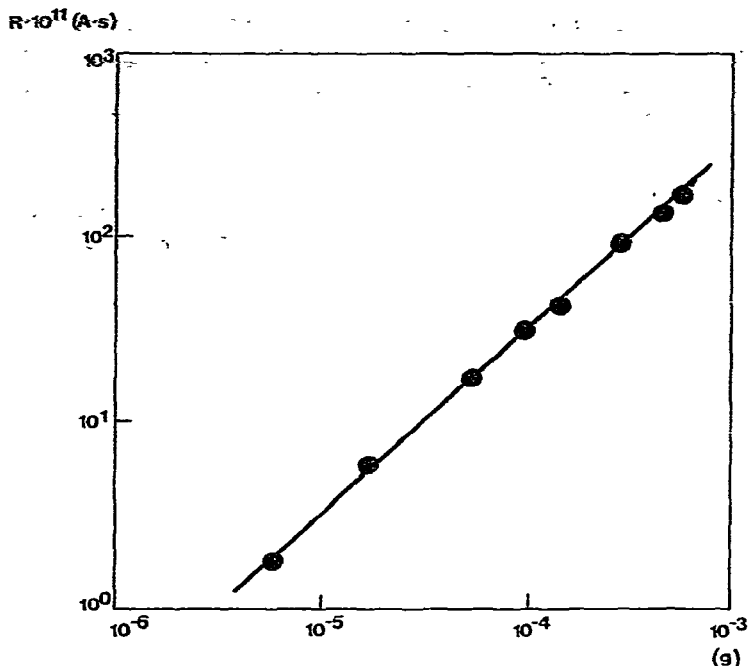
Fig. 5. Dependence of the response (R) of the electrokinetic detector shown in Fig. 3b on the amount of *m*-nitroaniline injected into the chromatographic column. Mobile phase, *n*-hexane–isopropanol (85:15); flow-rate, 0.6 ml/min; Vibron M 33B-2 electrometer with a $10^9 \Omega$ input resistance; each point represents an average value of three measurements.

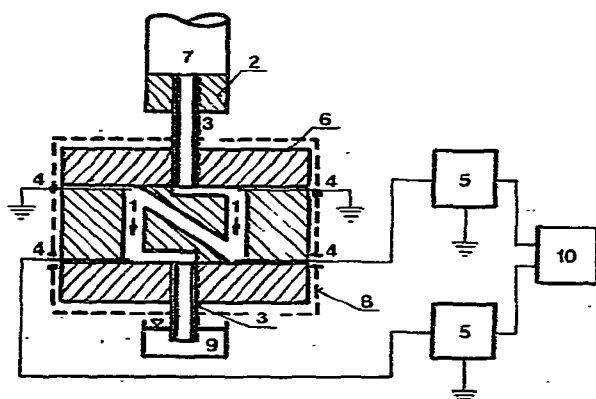Fig. 6. Schematic representation of the electrokinetic detector with two sorbent-packed cells as sensing elements. 1 = Cells packed with an adsorbent; 2 = PTFE seal of the column; 3 = PTFE capillary for the introduction and drain-off of the effluent; 4 = platinum contacts; 5 = electrometric amplifiers; 6 = PTFE body of the detector; 7 = column; 8 = earthed shielding; 9 = mobile phase waste; 10 = two-pen recorder.

A schematic representation of the electrokinetic detector with two cells filled with a sorbent is shown in Fig. 6. The cells, of length 2 mm and I.D. 1 mm, were drilled out in an electrically shielded PTFE block. The connecting channels directed the flow of column effluent through the cell with silica gel into the cell with pellicular alumina[32] and to the detector outlet. Both cells were earthed at the inlet of the liquid. The contacts for earthing and for the outlet of the current to the electrometric amplifier consisted of platinum wire of diameter 0.1 mm. The adsorbent was held within the cells by plugs of quartz-wool. The effect of the chemical nature of sorbent is apparent from Fig. 7, which shows chromatograms of nitroaniline isomers. The chromatograms reflect not only the different sensitivities of the two cells employed but also, with the water peak, an opposite polarity of the response.
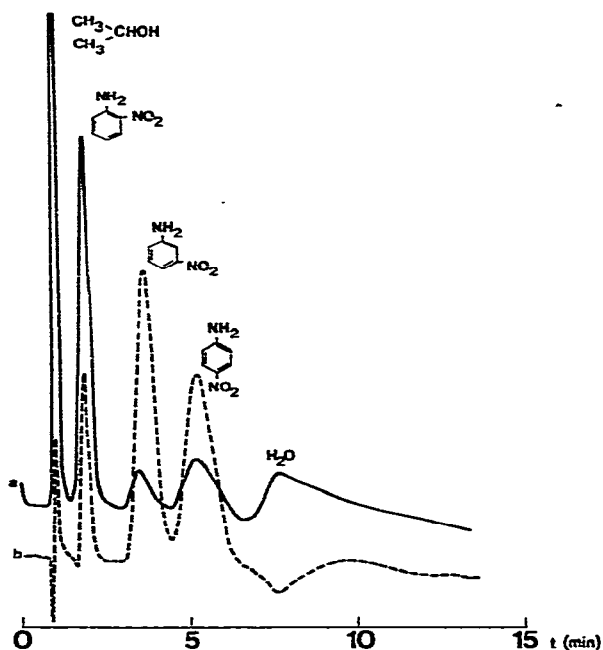

Fig. 7. Chromatogram obtained with the electrokinetic detector shown in Fig. 6 with the use of different sorbents packings in the cells. a, Silica gel, 12–25 μm (Lachema, Brno, Czechoslovakia); b, pellicular alumina, 10–20 μm (see ref. 32); mobile phase, n-hexane–isopropanol (85:15); sample, 0.3 mg of a mixture of nitroanilines dissolved in isopropanol.

The detection principle described can be used for mobile phases with an electrical conductivity of about 10^{-9} $\Omega^{-1} \cdot m^{-1}$ and less. This requirement is fulfilled with a large number of mobile phases, from paraffinic hydrocarbons, through aromatic and chlorinated hydrocarbons, to mixtures of hydrocarbons with alcohols, organic acids and bases. It can be assumed that the detection principle described might also be used with liquids of higher electrical conductivity, provided that a technique for measuring the streaming potential is employed.

The construction of the detector is very simple. The analytical property employed is the streaming current, which is a directly measured response of the system.

The instantaneous response, I_{str}, is appreciably dependent on the flow-rate of the mobile phase, which has to be kept constant. The dependence of the response on the temperature of the detection system is insignificant. The arrangement belongs to the category of non-selective detectors and is not suitable for gradient techniques.

LIST OF SYMBOLS

a	tube radius	m
C_+, C_-	concentration of positive or negative ions	$mole \cdot m^{-3}$
C_0	concentration of discharging ion in bulk of fluid	$mole \cdot m^{-3}$
C_s	concentration of discharging ion at boundary	$mole \cdot m^{-3}$
c_i	concentration of non-electrolyte species i	$mole \cdot m^{-3}$
$c_{s\,i}$	surface concentration of non-electrolyte species i	$mole \cdot m^{-2}$
$c_s^0{}_i$	monolayer capacity for species i	$mole \cdot m^{-2}$
D	molecular diffusivity of charge	$m^2 \cdot sec^{-1}$
d_p	particle diameter	m
F	Faraday number	$96,500\ A \cdot sec \cdot mole^{-1}$
F_m	volume flow-rate	$m^3 \cdot sec^{-1}$
h	mass-transfer coefficient	$m \cdot sec^{-1}$
I_{str}	streaming current	A
I_0, I_1	Bessel functions of the first kind of order zero and one, respectively	
K_d	distribution constant	m
l	length of capillary	m
n_+	transfer number of cation	dimensionless
q	charge density	$A \cdot sec \cdot m^{-3}$
q_{av}	charge density averaged over the tube radius	$A \cdot sec \cdot m^{-3}$
q_s	charge density at the boundary	$A \cdot sec \cdot m^{-3}$
R	gas constant	$8.31\ V \cdot A \cdot sec \cdot mole^{-1} \cdot {}^\circ K^{-1}$
Re	Reynolds number, $\bar{u}d_p/v$	dimensionless
r	spatial variable in radial direction	m
s	specific surface area	m^{-1}
Sc	Schmidt number, v/D	dimensionless
T	absolute temperature	$^\circ K$
u	local flow velocity	$m \cdot sec^{-1}$
$\bar{u}$	average flow velocity	$m \cdot sec^{-1}$
x	spatial variable normal to boundary	m
y	spatial variable in axial direction	m
δ	effective thickness of diffusion layer, $\delta = D/h$	m
ε	permittivity of liquid, $\varepsilon = \varepsilon_r \varepsilon_0$	$A \cdot sec \cdot V^{-1} \cdot m^{-1}$
ε_0	permittivity of free space	$8.854 \cdot 10^{-12}\ A \cdot sec \cdot V^{-1} \cdot m^{-1}$
ε_r	relative permittivity of liquid	dimensionless

ζ	zeta potential	V
θ_i	coverage of boundary with species i	dimensionless
κ	Debye–Hückel reciprocal distance	m^{-1}
$\varkappa$	conductivity of liquid	$A \cdot V^{-1} \cdot m^{-1}$
ν	kinematic viscosity of liquid	$m^2 \cdot sec^{-1}$
τ	relaxation time of liquid	sec
φ	potential	V
φ_d	electric potential at the outer Stern plane	V
φ_0	thermodynamic potential	V
φ_i	potential at the outer Stern plane of boundary covered with monolayer of species i	V

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