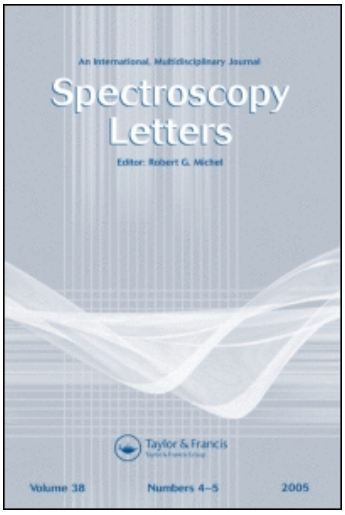

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Electrical Mobility Magnetic Resonance Spectroscopy (EMMRS)

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ELECTRICAL MOBILITY MAGNETIC RESONANCE SPECTROSCOPY (EMMRS)

KEY WORDS: electrical mobility, magnetic resonance, phase sensitive detection, charge carriers, ions, free radicals, protons, condensed matter, molecular dynamics

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ABSTRACT

A method to determine electrical mobility of charge carriers containing paramagnetic elements is presented. The motion-induced phase shift of the transverse magnetization component is observed by magnetic (nuclear or electron) resonance (MR). In fluid media, this method can determine the type of carriers and respective motion, lifetimes distribution, thermal and frequency dispersion of the mobility, translational relaxation rate and activation energies of these processes.

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INTRODUCTION

The transport of electrically charged elements (such as electrons, protons, ions and free radicals) is one of the essential processes influencing information and energy transfer, mass transport, molecular structure and dynamics in numerous abiotic and biological fluid media. Many physiological processes are strongly affected by the presence and transport rate of such elements. Proton transfer concerns physics, chemistry and biochemistry [1]. It has become obvious that ions participate not only in a simple diffusive motion in the course of cell metabolism. This also can concern the motion of large protein bound to free radical [1-3], as well as of ions such as H^+ or Ca^{2+} [4-6]. In many cases it seems that ions are not carried efficiently, but are liberated thanks to energy transfer initiated by signals [7]. The motion of ions frequently appears to be only concomitant with energy transfer along the conducting line. Therefore a direct observation of ionic mobility could contribute to the elucidation of mechanisms such as e.g. electric conduction in biological systems, proton conduction [7], information and charge transfer through cellular membranes [7] and the "calcium wave" [8]. That can also concern the mechanism of interaction between biological systems and electromagnetic fields, leading to the explanation of processes which are crucial as regards the physiology and pathology of a cell and possible therapeutic effects [9-11]. Several methods have been worked out for indirect detection of free radicals [12,13]. None of them, however, can serve for the determination of the dynamics of their motion.

The present work demonstrates the theoretic possibility of measuring the electrical mobility of charge carriers containing paramagnetic elements (paramagnetic nuclei or unpaired electrons) by phase-encoding gradient modulation in nuclear (NMR) or electronic (ESP) magnetic resonance. The motion-induced phase shift acquired by spins moving along a magnetic field gradient is used [14-16]. We are considering the effects induced by homogeneous external electric field [17,18]. The method proposed is based on the previously demonstrated methods of measuring displacement caused by an elastic wave [19-22] or magnetic field gradient [23-25].

METHOD

According to Kohlraush law, an electric field $E(t)$ applied to a fluid of viscosity η containing carriers with charge q and effective radius a, causes their displacement $\xi(t)$ which, when taking into account Stokes description of internal friction forces in a liquid, can be written as

$$\xi(t) = \frac{q}{6\pi\eta a}\int E(t)dt \qquad (1)$$

Consider the MR phase modulation integral arising from a temporally modulated magnetic field gradient, $G(t)$, during the time interval t to $t + \delta$ [14-16]

$$\Delta\Phi = \gamma \int_{t}^{t+\delta} \bar{G}(t).\bar{r}(t)dt \qquad (2)$$

where γ is the gyromagnetic ratio of paramagnetic elements into the charge carriers for which phase changes in the transverse magnetization component, $M_{\perp}$, are measured, and $\bar{r}(t)$ is the time-dependent position of these paramagnetic elements, with a modulation of the magnetic field gradient $G(t)$ accomplishing the independence of $\Delta\Phi$ upon spatial coordinates $\int_{t}^{t+\delta} \bar{G}(t)dt = 0$. This condition is satisfied by every bipolar periodic function $G(t)$ with a duration time δ equal to the integral multiple of its period T ($\delta \equiv NT$, where N = 1,2,3 ...). According to equation (2), it is possible to transform the displacement of charge carriers to the phase change of the transverse magnetization component, $M_{\perp}$, of paramagnetic elements contained in the carriers. In order to avoid electric polarization and the effect of charge separation in the medium, it seems purposeful to use an time varying electric field, $E(t)$. In view of slow-changing slopes, the function allowing to neglect, in first approximation, the effects related to the inertia of the displaced charge carriers is a sinusoidal time dependence of the field intensity $E(t)$. The slowness of changes in the slopes of time

dependencies, $E(t)$ and $G(t)$, is also important for reducing the inductive effects. In addition, in this case the spectrum (Fourier transform) of the gradient is simple [14]. The phase change of component M_1 of paramagnetic elements contained in the observed charge carriers in a sinusoidal time-variable electric field, $E(t)$, with angular frequency ω_E and amplitude E_o in the magnetic field B_o, with the superimposed magnetic field gradient $G(t)$, sinusoidally time-variable, with angular frequency ω_G and amplitude G_o is

$$\Delta\Phi(\alpha,N) = \frac{F}{2\pi N(1-\alpha)}\left\{\cos\varphi - \cos\left[2\pi N(1-\alpha)+\varphi\right]\right\} \qquad (3)$$

where $F = \frac{2\rho\gamma N\vec{G}_o.\vec{E}_o}{\omega_E\omega_G}$, $\alpha = \omega_E/\omega_G$, and $\rho = \frac{q}{6\pi a\eta}$ denotes the mobility of charge carriers, and φ is the phase difference between $E(t)$ and $G(t)$.

Phase changes $\Delta\Phi(\alpha,N)$ described by equation (3) display several interesting physical features: (i) they are a resonance character. Figure 1 shows the normalized functions $\Delta\Phi(\alpha,N)/F$ for several values of the phase shift, φ. The resonance condition is obvious ($\omega_E = \omega_G$), but it creates possibility to achieve high signal-to-noise ratio; (ii) their value is a linear function of the scalar product $\vec{G}_o \bullet \vec{E}_o$. Hence, the change in the orientation of G_o enables the spatial distribution of the tensor of charge carrier's displacement in an anisotropic media to be measured; (iii) in the case of simple isotropic media, its maximum corresponds to a phase shift between $E(t)$ and $G(t)$ of $\varphi = (1/2 \pm n)\pi$, where $n = 0, 1, 2 \ldots$ In the case of complex systems (e.g. biological tissues), the precise measurement of phase shift φ will make possible the determination of time constants of electrical relaxation of charge carriers (such as ions or free radicals in ionic or radical „waves"); (iv) they are accumulated during many periods of changes in the $G(t)$ sequence, thus enabling the dynamics of the motion of charge carriers to be measured in a wide range of both qualitative (different kinds of carriers) and quantitative (different mobilities of carriers of the same type) changes; (v) they are linear functions of electric field intensity amplitude E_o. Therefore, their

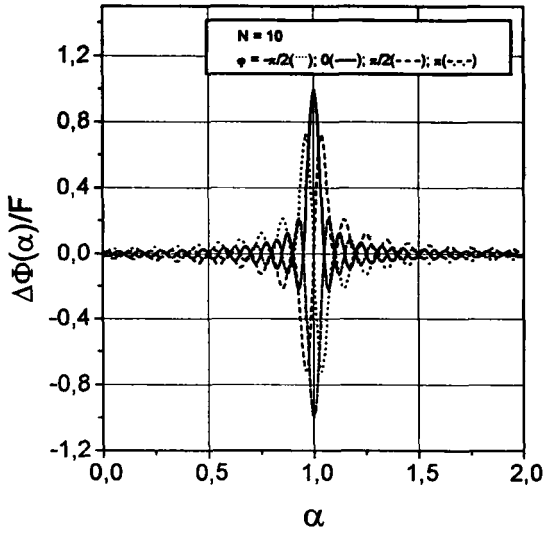

Fig. 1. Normalized function $\Delta\Phi(\alpha,N)/F$ for several values of the phase shift φ between $E(t)$ and $G(t)$ [φ = $-\pi/2$ (····); 0 (—); $\pi/2$ (——); π (—·—·—)].

simple mutual transformation is possible and, hence, the measurement range (field of view - FOV [14]) can be improved, for example by changing both quantities or fixing the phase changes $(\Delta\Phi)_0$ and sweeping the spectrum of charge carriers mobility with the amplitude change of the electric field, E_0.

DISCUSSION

The measurement of the mobility of charge carriers practically consists in recording the changes in the transverse magnetization component, $M_\perp$, caused by the displacement of spins together with the charge carrier, induced by the electric field $E(t)$. Figure 2 shows the suggested pulse sequence to be used. On the scale of the phase changes in the transverse magnetization component, $M_\perp$, the spectrum obtained comprises lines with intensities proportional to the concentration of the respective

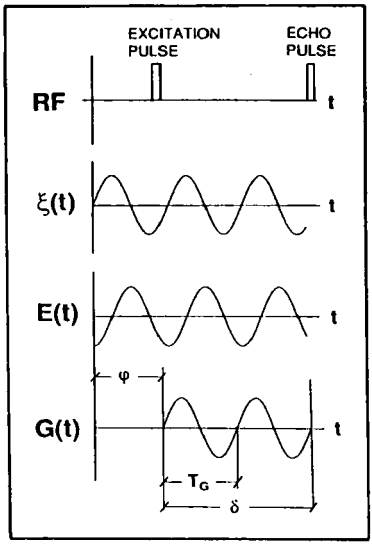

Fig. 2. Proposed pulse sequence.

types of carriers with different mobilities. The positions of these lines correspond to the value of the mobility

$$\rho_i = \frac{v_i}{E} = \frac{q_i}{6\pi\eta a_i} = \frac{(\Delta\Phi_i)_{max}\omega_E\omega_G}{4\pi\gamma_j N\vec{E}_o.\vec{G}_o} \qquad (4)$$

where the subscript *i* refers to the type of the charge carrier, *j* corresponds to the type of the involved paramagnetic element determining the MR response, and *max* means that the change in the phase of transverse magnetization component assumes a maximum value under the conditions of the experiment (i.e. for synchronized runs of *E(t)* and *G(t)* and the optimum choice of the phase shift [see point (ii) in the previous section]). By combining the studies on the dynamics of the motion of charge carriers and the observation of its MR spectrum, their identification is possible in many situations and the direction of the phase changes enables the sign of the carried electric charge to be determined.

The currently used phase sensible detectors (PSD) can detect phase changes in a relatively narrow interval, i.e. from - π to π. The broadening of this scale is simple in the case of the mobility of the first kind, i.e. in such an E_o changes range in which the mobility is independent of the E value. Then, in view of the linear dependence of $\Delta\Phi$ upon E, the mutual transformation of spectra between scales $\Delta\Phi$ and E is possible [see point (iv) in the previous section]. Broad range variations in the electric field intensity, E_o, reveal regions in which: (a) the type of the mobility of charge carriers changes, (b) the electric field induces the release of ions or free radicals, and (c) the electric field induces ionic or radical waves.

Having regard to lifetimes of charge carriers, several specific cases can be distinguished in the phase change measurements, $\Delta\Phi(\alpha,N)$:

I. Stable charge carriers: Long-lived changes occurs when the lifetimes τ markedly exceed the duration time of the sequence $G(t)$, $\delta = NT_G$. Then, relation (3) describes the phase changes in the transverse magnetization component in a time interval δ markedly shorter than spin-spin, $T2$, relaxation times. The broadening of individual lines in the spectrum provides additional information on the share of other types of motion in the transport of charge carriers, such as their diffusion. The calculation shows that the diffusion displacements during a time of 0,1s at ambient conditions and the displacements forced by electrical field of the ions in aqueous solutions are in the same order at the electrical field intensity of the order of (1 ÷ 5) V/cm. Time evolution of the line intensity provides information on the MR relaxation rate, in particular on $(T2)^{-1}$.

II. Charge carriers generated by pulse sources (e.g. those injected into the sample, ions liberated by an electric pulse or generated by an ionizing radiation pulse), with lifetimes, τ, shorter than the duration time of the sequence $G(t)$, $\delta = NT_G$. During the $G(t)$ sequence, the concentration of charge carriers changes (e.g. due to recombination or charge transfer). Hence, their displacement only lasts for the time τ. Time evolution of the spectra can therefore provide information on lifetimes τ and the distance travelled. The integration in equation (2) is over lifetimes τ. Equation (3) can therefore be written as

$$\Delta\Phi(\alpha,N,n,\tau)=\frac{F}{2\pi N(1-\alpha)}\left\{\cos\varphi-\cos\left[2\pi\nu_G(1-\alpha)\tau+\varphi\right]\right\} \qquad (5)$$

where n denotes the population of carriers with lifetime τ.

As a result, phase change distribution determined by the distribution of charge carriers lifetimes is obtained. In resonance, i.e. for (α = 1), $\Delta\Phi(\alpha,N,n,\tau)/F$ is a linear function of charge carriers lifetime, τ, thus correctly reflecting their distribution in the sample. If, in addition, the G(t) sequence duration time is considerably shorter than relaxation times *T1* and *T2* ($\delta << T1,T2$), the phase dependence of the line intensity $I[\Delta\Phi(\alpha,N,n,\tau)]$ determines the time dependence of the concentration of the type of charge carriers dealt with. Getting an insight into the phase changes distribution makes possible the determination of the dynamics of processes responsible for the charge transfer between the generated carriers and their environment. In the simplest case, i.e. charge recombination of one type, the lifetime distribution is exponential and the phase change is described by a monoexponential function. In more complex systems, the function $\Delta\Phi(\alpha,N,n,\tau)/F$ can assume either the shape of multiexponential functions, for charge carriers that can participate in several mechanisms of charge transfer with continuous distribution of lifetime τ, or is bell-shaped in the case of discrete values of lifetimes τ_i. The above discussion applies also to dynamic systems in which charge carriers with lifetimes shorter than the *G(t)* sequence duration time are generated continuously or periodically. The proposed method can find application in investigations of chemical or biochemical reactions, in which free radicals or ions are formed in particular steps (e.g. in Haber-Weiss reaction [6] or aerobic oxidative process [26]). This seems of particular interest in the studies on the information transfer in neurone cells, Na/K ion pumping through cellular membranes, or proton currents in water bound to different types of proteins. Proportionality of line intensity to the current charge carriers concentration enables the dynamics of their transformation to be estimated. The possibility of phase separation of MR response originating from charged and unchanged elements raises

hopes to obtaine the MR signal from charged elements with low concentration. The possibility to change frequencies ω_E and ω_G opens up prospects for studying translational relaxation of particular types of charge carriers. The dispersion of mobility, ρ_i, should make possible the determination of translational relaxation times and their distribution. The knowledge of the temperature dependence of mobility, dispersion regions and lifetimes, τ, of charge carriers affords possibilities for the determination of activation energies of these processes. The measurement of these quantities seems worthwhile in both fundamental research and applications, e.g. in hyperthermia [27-29], radiotherapy [30] or diagnostics of energy expenditure physiology in mitochondria [13,31]. One of the parameters named above can be a good thermometric indicator to be used in hyperthermia [28,32]. In addition, the measurement of the displacement of charge carriers provides information on the microviscosity of the medium in which the motion occurs [33].

The combination of the presently discussed method and the previously proposed methods of measuring the displacement of the elements of the matter, induced by an elastic wave generated either by external or internal sources [19-22], and displacement of paramagnetic elements induced by a strong magnetic field gradient [23-25] seems also promising. Such a combination will afford possibilities of complementary investigations, as well as of a mutual scaling procedure.

CONCLUSIONS

The method of electrical mobility MR spectroscopy (EMMRS) enables spectra of charge carriers mobility to be obtained, thus providing information on: (a) the type of charge carriers and motion they are involved in, (b) the type and mobility of carriers generated or released in physico-chemical and biological processes, (c) lifetimes, thermal and frequency dispersion of mobility, translational relaxation rate and activation energies of these processes for different types of carriers, stabile, generated or released in the sample, (d) microviscosity of the medium in subregions

of the sample in which charge carriers are localized (e.g. in mitochondria, cellular nuclei, water when free or bound to biopolymers).

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