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Integral Doppler anemometry in porous membranes for the analysis of liquid mixtures and examination of membrane properties

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ABSTRACT

The possibility of field flow fractionation (FFF) using integral Doppler anemometry (IDA) in the pores of transparent membranes is theoretically examined. The IDA spectra were calculated for cylindrical pores, where a transverse force exists owing to the electrical field of the double electrical layer on the pore walls. Two possibilities were considered: (a) particles are repulsed from the wall and focused near pore axis, and (b) they are attracted to the wall and concentrated in its vicinity. The IDA spectra are essentially different in these cases and this circumstance may be the basis for programming analyses of liquid mixtures containing ampholytic particles. It is shown that FFF in pores is possible if the pore-size distribution is narrow enough. If the pore-size distribution is broad, IDA can be used for the investigation of this distribution. It is also shown that such an investigation is most convenient if particles are focused near the pore axis. In this case IDA spectra averaged over a large number of pores are especially simply linked to the pore-size distribution and do not depend on the interaction of a particle with an electrical field in a pore.

INTRODUCTION

The application of correlation spectroscopy to studies of liquid mixture in a laminar flow and a transverse force field has been proposed [1–3] and a clear dependence of averaged spectra of scattering on the transverse particle distribution has been shown. This distribution is due to the interaction of particles with a transverse force field and to thermal motion. As a result of theoretical examination, the experimental method of analytical field flow fractionation (FFF) called integral Doppler anemometry (IDA) has been developed. The main features of IDA are continuous injection of the sample mixture and a short time of analysis, approximately equal to the time of relaxation in FFF [4–6]. However, a further decrease in analysis time is very desirable, especially in programming processes of analysis. For this purpose channels with a small transverse size are necessary.

THE MATHEMATICAL PROBLEM

Porous membranes containing pores transparent to light may be a suitable system for IDA. For example, nuclear filters may be used; basically they represent polymer films, in which pores are produced by the action of heavy ions in accelerators of electrically charged particles. These membranes may have positive or negative surface electrical charge at different pH values. The transverse electrical field in the pores causes redistribution of the charged particles driven by flow through the pores. The IDA spectra, depending on the transverse distribution of particles, may provide information about the properties of particles and also the properties of the pores and membrane surface. For particle examination it is necessary to use calibrated pores. For example, nuclear filters with an average pore size of 0.5–2.0 μm with a pore size dispersion of about 5% may be used. In this case the main problem is the

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calculation of IDA spectra in a cylindrical capillary, where transverse force and laminar flow exist. As in a flat channel, the spectrum of scattering on a single particle can be considered as

$$S_0(\omega) = \delta(\omega - qu) \quad (1)$$

where ω is frequency, q is the wave vector of scattering (difference between the wave vectors of the initial and scattered light) and u is the velocity of the scattering particle. Eqn. 1 can be used at $u \gg qD$, where D is the diffusion coefficient of the particle. Usually these parameters are $q \approx 10^4$ cm^{-1} and $D \lesssim 10^{-6}$ cm^2/s, tha is, u must be $\gg 10^{-2}$ cm/s. Because all particles scatter laser light independently, the integral spectrum of scattering averaged over the cross-section of the channel can be written as

$$S_1(\omega) = 2\pi \int_0^R r\mathrm{d}r W(r) S_0[\omega - qu(r)] \quad (2)$$

where r is the distance from the axis of the capillary, $W(r)$ is the probability of finding a particle at distance r, $u(r)$ is the flow profile in the capillary and R is the pore radius. If we neglect electroosmotic flow, the flow profile can be considered as

$$u(r) = u_0[1 - (r/R)^2] \quad (3)$$

where

$$u_0 = \Delta p R^2 / 4\eta h \quad (4)$$

is the maximum flow velocity, Δp is the pressure difference at the membrane applied, η is the viscosity of the liquid and h is the thickness of the membrane. Substituting eqn. 1 in eqn. 2, we find that

$$S_1(\omega) = 2\pi r(qu) W[r(qu)]\ \mathrm{d}r/\mathrm{d}(qu)|_{qu=\omega} \quad (5)$$

where

$$r(qu) = R(1 - qu/qu_0)^{1/2} \quad (6)$$

according to eqn. 3. The probability $W(r)$ is considered as a Boltzmann distribution:

$$W(r) = \mathrm{e}^{-qf(r)/kT} / \int_0^R 2\pi r\mathrm{d}r \mathrm{e}^{-qf(r)/kT} \quad (7)$$

where q is the effective electrical charge of a particle, $f(r)$ is the potential of the double electrical layer in the pore and kT is the thermal energy. Usually the energy of electrostatic interaction in double electrical layers is about 10 kT. Therefore, the distribution in eqn. 7 must be very narrow: particles repulsed from the pore wall are focused near its axis and attracted particles are concentrated in the vicinity of the wall. In the former instance eqn. 7 can be written as

$$W(r) = [E_0 \mathrm{e}^{-E_0(r/R)^2}]/\pi R^2 \quad (8)$$

and in the latter as

$$W(r) = [E_0 \mathrm{e}^{-E_0(R-r)/R}]/2\pi R^2 \quad (9)$$

where $E_0 = \alpha q f_0/kT$, $\alpha \approx 1$ and f_0 is the potential of the double electrical layer. The coefficient α is defined by the distribution of potential, $f(r)$; for example, if this distribution is parabolic, $\alpha = 1$ in eqn. 8 and $\alpha = 2$ in eqn. 9. Substituting eqns. 6 and 8 in eqn. 5, we find that

$$S_1(\omega) = [E_0 \mathrm{e}^{-E_0(1-\omega/qu_0)}]/qu_0 \quad \text{if } \omega \leqslant qu_0$$
$$S_1(\omega) = 0 \quad \text{if } \omega > qu_0 \quad (10)$$

for particles focused near the axis of the pore. The spectrum represenred by eqn. 10 has an asymmetric peak which has a tail of width *ca.* qu_0/E_0 (see Fig. 1). The maximum of this peak is at $\omega = qu_0$. The spectra of particles with different charges q must have different widths and the general spectrum of mixture containing these particles can be a source of information about the particle charges.

The velocities of particles attracted to the wall are much less than u_0 and instead of eqn. 6 we can use the aprpoximate expression

$$r \approx R(1\text{–}2qu/2qu_0) \quad (11)$$

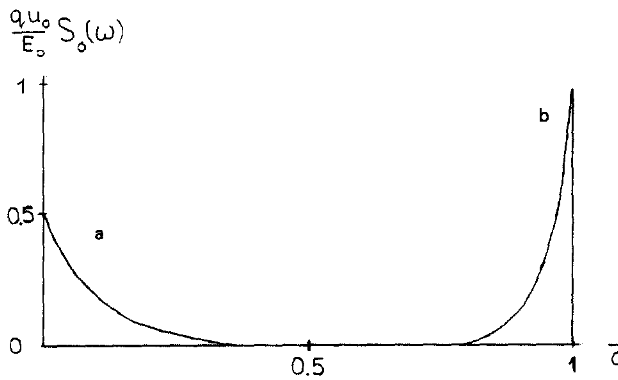

Fig. 1. IDA spectra in a cylindrical capillary: (a) particles attracted to the wall; (b) particles focused near the axis. $E_0 = 20$.

Substituting eqns. 9 and 11 in eqn. 5, we find that

$$S_1(\omega) = (E_0 e^{-E_0\omega/2qu_0})/2qu_0 \qquad (12)$$

The IDA spectrum of attracted particles occurs at $\omega \approx 2qu_0/E_0 \ll qu_0$ and has a qualitatively different shape than the spectrum represented by eqn. 10 (see Fig. 1). The difference between the spectra of attracted and repulsed particles can constitute the basis for a programmed analysis of mixtures containing ampholytic particles. This process may be controlled by programmed pH changes with concomitant changes in particle charge. Of course, changes in the potential distribution, $f(r)$, must be small or known at any pH. The IDA spectrum with a uniform transverse particle distribution will be used in further considerations. It has been calculated [7] and has a rectangular shape:

$$S_1(\omega) = qu_0 \quad \text{if } \omega \leqslant (qu_0)^{-1} \qquad (13)$$

$$S_1(\omega) = 0 \quad \text{if } \omega > (qu_0)^{-1}$$

Usually a large number of pores are simultaneously illuminated by laser light. If the pore-size distribution is narrow, the observed spectrum is still described by eqns. 10 and 12. However, if the pore-size distribution is broad, the IDA spectrum observed on unit area of the membrane must be written as

$$\langle S_1(\omega)\rangle = N_0 c_0 h \int_0^\infty S_0[\omega, E_0, q\Delta pR^2/4\eta h]\pi R^2 n(R)\mathrm{d}R \qquad (14)$$

where $n(R)$ is the pore-size distribution normalized in the following way:

$$\int_0^\infty n(R)\mathrm{d}R = 1$$

c_0 is the concentration of particles scattering laser light, N_0 is the number of pores in unit area of the membrane and h is the thickness of the membrane. Eqn. 4 for the maximum flow velocity u_0 is used in eqn. 14; the spectrum of scattering on a single particle is also normalized per unit area, similarly to eqn. 1. It is taken into account also that the IDA spectrum in any pore is proportional to the number of particles present, which is equal to $c_0\pi R^2 h$. Eqn. 14 can be expressed in another way using the pore distribution according to the cross-sectional area, σ, $n^*(\sigma)$:

$$\langle S(\omega)\rangle = N_0 c_0 h \int_0^\infty S_0[\omega, E_0, \omega_0(\sigma/\sigma_0)]\sigma n^*(\sigma)\mathrm{d}\sigma \qquad (15)$$

where $\sigma_0 = \Delta p/4\eta$ and $\omega_0 = \pi q/h$. The averaged IDA spectrum gives the possibility of finding pore distributions $n(R)$ and $n^*(\sigma)$ by solving integral eqns. 14 and 15. In some situations, however, the relationship between $\langle S_0(\omega)\rangle$ and the pore distributions $n(R)$, $n^*(\sigma)$, can be simplified. For example, if particles are focused near the pore axis. The IDA spectrum of this single pore has the shape of a narrow peak, the width of which is more or less equal to the dispersion of pore distribution $n^*(\sigma)$. In this case a "unit" spectrum $S_0(\omega)$ in eqn. 15 can be expressed as

$$S_0(\omega) = \delta[\omega - \omega_0(\sigma/\sigma_0)] \qquad (16)$$

Substituting eqn. 16 in eqn. 15, we obtain the following expression for the averaged IDA spectrum:

$$\langle S_0(\omega)\rangle = N_0 c_0 h(\sigma_0/\omega_0)^2 \sigma n^*(\sigma)|_{\sigma=\sigma_0(\omega/\omega_0)} \qquad (17)$$

Eqn. 17 shows that focusing of particles near the pore axis simplifies the problem: the registered averaged IDA spectrum permits the pore distribution $n^*(\omega)$ to be reconstructed immediately. The second advantage of these conditions is the weak dependence of the averaged spectra on the details of the particle interaction with the electrical field in the pores: eqn. 17 does not contain the parameter E_0. This indicates that calibrated particles are not necessary for measurement, it is only necessary to use particles focusing near the pore axis. These conditions may be realized if $E_0 \gg 1$ and if the width of the pore distribution $n^*(\sigma)$ is $\gg E_0^{-1}$. A similar situation arises with a uniform transverse distribution of particles in the pores if they are uncharged or there is no electrical field. Substituting eqn. 13 into eqn. 15 and taking derivatives, we find that

$$\mathrm{d}[\langle S(\omega)\rangle]/\mathrm{d}\omega = N_0 c_0(\sigma_0/\omega_0)^2 n^*(\sigma)\sigma|_{\sigma=\sigma_0(\omega/\omega_0)} \qquad (18)$$

Eqn. 18 shows that the distribution $n^*(\sigma)$ can be obtained from averaged IDA spectra relatively simply if the particles are uniformly distributed across the pores.

Next, it is necessary to determine the limits of approximations used in the calculations and the conditions necessary to carry out informative experiments. The time of transverse relaxation in an electrical field to a Boltzmann distribution, $\tau_\perp$, must be much less than the time for a particle to passing through the pore, $\tau_\parallel$. The time of relaxation, $\tau_\perp$, is *ca.* R^2/E_0D. E_0 can be evaluated as bf_0/D, where b is the electrophoretic mobility. If the particle size is about 10^{-5} cm, usually $b \approx 10^{-4}$ cm^2/V · s and $D \approx 10^{-7}$ cm^2/s. The characteristic value of the surface potential is *ca.* 10^{-1} V. Hence $E_0 \approx 100$ for such particles and the time of transverse relaxation $\tau_\perp \approx 10^{-3}$–$10^{-2}$ s if the pore radius R is about 10^{-4} cm. The time of passing $\tau_\parallel$ is *ca.* h/u_0. Usually h is about 10^{-2} cm and the velocity u_0 satisfying the condition $u_0 \gg qD$ is about 10^{-2} cm/s. Under these conditions $\tau_\parallel \approx 10\tau_\perp$ and a Boltzmann distribution of particles is established along the whole pore length. According to eqn. 4, these flow velocities need a pressure gradient across the membrane of $\Delta p/h \approx 10^4$ g/cm^3. This value is comparable to the pressure gradient across a horizontal membrane due to the force of gravity.

CONCLUSIONS

Registration of averaged IDA spectra of particles driven by flow through a transparent membrane can provide a source of information about the particle charge distribution and their dependence on pH if the pore-size distribution is narrow. The investigation of porosity parameters determining the selectivity of membrane separation processes is possible if the pore-size distribution is broader. In the latter instance the shape of the averaged IDA spectrum is particularly simply related to the pore-size distribution if particles are focused near the pore axis. The data obtained by a pure hydrodynamic process of particles passing through pores can give the most direct information about the parameters determining membrane selectivity.

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