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Diffusion and $1/f$ Noise

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Summary. The noise associated with ion transport through porous membranes is considered as a diffusion process. This is confirmed experimentally by measuring the noise spectra associated with pores of known dimension. It is then shown that one dimensional diffusion through pores of variable length can produce approximate $1/f$ noise spectra, if the distribution of lengths is proportional to $(\text{length})^{-1}$.

For approximately ten years, membrane transport has been studied by means of the noise spectra generated during the transport process. These studies were reviewed by Verveen and de Felice (1974). Many of the results showed $1/f$ power spectra. There has, recently, been a general revival of interest in $1/f$ noise. It has been studied extensively by Hooge and coworkers (Hoppenbrouwers & Hooge, 1970; Hooge & Gaal, 1971), and has been one of the forms of noise spectrum found in nerve membranes, squid axon (Fishman, 1973), lobster axon (Poussart, 1971), and node of Ranvier of frog (Siebenga & Verveen, 1972). Recently, Dorset and Fishman (1975) published a study of $1/f$ noise in various artificial types of porous membranes; most of the membranes they studied had heterogeneous pores, but one type (mica, their Fig. 6) contained pores of constant, known dimensions. This membrane gave a power spectrum steeper than f^{-1}, and close to $f^{-1.5}$ if correction is made for background. Since, as we shall see, diffusion produces an $f^{-1.5}$ spectrum, this is an interesting fact.

Diffusion as a source of noise has likewise been extensively investigated. Surface diffusion, out of circular patches or long straight patches, was investigated theoretically by MacFarlane (1950) and corrected by Burgess (1953). Together, their papers showed that at "high" frequency, the power spectrum associated with diffusion fell as $f^{-3/2}$, leveling off logarithmically at "low" frequencies. The high frequency $f^{-3/2}$ behavior was shown by Lax and Mengert (1960) to be universal. The boundary between low and high frequency, as we shall see below, is actually at quite low frequency, in most cases. The field was reviewed by van Vliet and Fassett (1965).

In this paper, we are primarily concerned with one dimensional diffusion. We examine experimentally the noise spectra obtained when a current is passed through a membrane containing pores of known dimensions. We also show that one-dimensional diffusion through pores of varying length should give approximately f^{-1} noise power spectra.

Materials and Methods

Measurements of noise spectra were made on Membra-Fil (Johns-Manville Corp.) polycarbonate membranes. Each membrane has pores of fixed diameter ($\pm 10\%$), with the maximum diameters of the pores in the membranes used here, and the corresponding pore densities, being 0.6 µm (3×10^7 pores/cm^2), 0.8 µm (3×10^7 pores/cm^2), 3.0 µm (2×10^6 pores/cm^2), and 5.0 µm (4×10^5 pores/cm^2). Nominal membrane thickness was 10 µm, and average pore diameter 0.9 of the maximum value listed.

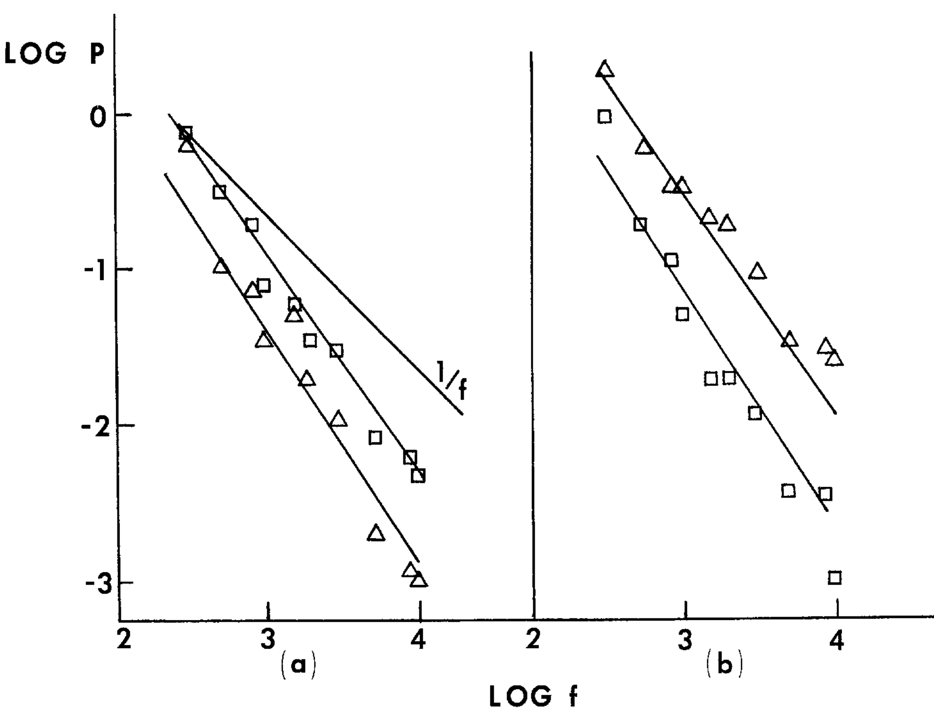

Fig. 1. Spectra of transport through pores, corrected for background: (a) □, 0.6 µm pore, current density 640 A/m^2, △ 0.8 µm pore current density 640 A/m^2 (b) □, 3.0 µm pore; current density 600 A/m^2, △ 5.0 µm pore, current density = 640 A/m^2. In each case, points are experimental, line is drawn to have theoretical −1.5 slope. In (*a*) a $1/f$ line is included for comparison. Power is in arbitrary units

A four electrode voltage noise measurement method was used, the two outer electrodes providing constant current (regulated by a 100 kΩ potentiometer), the two inner electrodes serving as measuring electrodes. All four electrodes were platinum. The electronics were the same as previously used (Green, 1973). Briefly, the noise was taken past a high pass filter to remove dc, and was then amplified 60 db by an Applied Cybernetics LA460V low noise amplifier. The noise was then analyzed by a Tektronix 3L5 spectrum analyzer. The spectra were not scanned, but measured point by point, two points to the octave. The recorder output of the 3L5 went to a Keithley 610B electrometer, from which it was read. The frequency response of the 3L5 was checked with an IEC F34 function generator, and the spectral response checked for constancy with a General Radio 1390B noise generator.

Background spectra were taken immediately before and/or after each spectrum. The battery was left connected, and the current density reduced to approximately 6 A/m^2, from the approximately 600 A/m^2 used during the run (*see* Fig. 1). In this manner, conditions remained reliably constant between run and background. The electrolyte used was 0.06 M NaCl, and the resistance of the cell (including membrane) was less than $2\times10^3\,\Omega$ in all instances. Membra-fil membranes being hydrophilic (according to the manufacturer), pore filling was not a problem. This is further attested to by the effective identity of results among membranes with pores of various sizes. Given the resistance of the membranes, no RC filter effect is expected, nor is any curvature of spectra found.

Results and Discussion

The spectra are shown, with lines corresponding to an $f^{-1.5}$ spectrum. As can be seen, an $f^{-1.5}$ spectrum is a far better representation of the spectrum than f^{-1}. This is a strong indication that diffusion through pores of uniform size is the transport mechanism; the formula for one dimensional diffusion is (van Vliet and Fassett, 1965; $G(\omega)$ is given as carrier concentration fluctuation spectrum)

$$G(\omega)=\frac{\langle c^2\rangle L^2}{D\,\theta^3}\left(1-e^{-\theta}(\cos\theta+\sin\theta)\right) \tag{1}$$

where $\langle c^2\rangle$ = mean square carrier concentration fluctuation. D = diffusion coefficient of the carriers, L = length of pore, and $\theta=L(\omega/2D)^{1/2}$, $\omega=2\pi f$. When $\theta\ll 1$,

$$G(\omega)\approx\frac{\langle c^2\rangle L^2}{D\,\theta}=\left(\frac{2}{D}\right)^{1/2}\langle c^2\rangle L/\omega^{1/2}, \tag{2a}$$

for $\theta\gg 1$

$$G(\omega)\approx\frac{\langle c^2\rangle L^2}{D\,\theta^3}=\frac{2^{3/2}\langle c^2\rangle D^{1/2}}{L\,\omega^{3/2}}. \tag{2b}$$

The spectrum thus changes from $\omega^{-1/2}$ at low frequencies to $\omega^{-3/2}$ at high frequencies. The boundary between low and high frequency is $\theta=1$, or $\omega = 2D/L^2$. For $L = 10\,\mu\text{m}$, $D = 10^{-9}\,\text{m}^2\,s^{-1}$, this gives $\omega = 20$, or $f \approx 3$ Hz. Actually measurable deviations from $\omega^{-1/2}$ and $\omega^{-3/2}$ behavior will begin some distance, perhaps an octave, from $\theta = 1$. For $L = 0.1\,\mu\text{m}$, the turnover frequency becomes $f \approx 30$ kHz. A mixture of lengths in the range $0.1 < L < 10\,\mu\text{m}$ would therefore produce spectra of slopes intermediate between 0.5 and 1.5 over much of the frequency range over which we normally measure.

It was shown by van der Ziel (1950) and, independently, by du Pre (1950) that an appropriate distribution of relaxation times could produce an f^{-1} spectrum. Following a similar method, it is possible to show that a proper distribution of diffusion lengths leads to an f^{-1} spectrum. From Eq. (1), which applies to a particular value of L, we can calculate the spectrum of a system with a distribution $q(L)$ of lengths according to

$$G(\omega) = \int_0^{\infty} G_L(\omega)\, q(L)\, dL \tag{3}$$

where $G_L(\omega)$ is the spectrum given by Eq. (1) for a particular value of L. Let us take

$$q(L) = \ln\left(\frac{L_{\text{max}}}{L_{\text{min}}}\right)^{-1} L^{-1} \quad \text{for } L_{\text{min}} < L < L_{\text{max}} \tag{4}$$

$$q(L) = 0 \quad \text{elsewhere}.$$

The distribution thus defined is normalized. If we attempt to integrate Eq. (3) directly, using the $q(L)$ defined in Eq. (4), we find an integral which can only be evaluated in series form. However, by using the high and low frequency approximations of Eq. (2), and treating the integral as though the two approximations each held all the way to $\theta = 1$, the integral becomes tractable. The error is not catastrophic; the approximations are poor only over about an octave in frequency, and then the correct formula would produce a spectrum close to f^{-1} in any case. We get, then

$$G(\omega) = \int_{L_{\text{min}}}^{(2D/\omega)^{1/2}} \left(\frac{2}{D}\right)^{1/2} \frac{\langle c^2 \rangle}{\omega^{1/2}} \frac{1}{\ln \dfrac{L_{\text{max}}}{L_{\text{min}}}}\, dL$$

$$+ \int_{(2D/\omega)^{1/2}}^{L_{\text{max}}} \frac{2(2D)^{1/2} \langle c^2 \rangle}{\ln \dfrac{L_{\text{max}}}{L_{\text{min}}}\, \omega^{3/2}} \cdot \frac{1}{L^2}\, dL, \tag{5a}$$

so,

$$G(\omega)=\frac{2\langle c^2\rangle}{\ln\dfrac{L_{\max}}{L_{\min}}}\cdot\frac{1}{\omega}-\frac{2^{1/2}}{D}\,\frac{\langle c^2\rangle L_{\min}}{\omega^{1/2}\ln\dfrac{L_{\max}}{L_{\min}}}$$

$$+\frac{2\langle c^2\rangle}{\ln\dfrac{L_{\max}}{L_{\min}}}\cdot\frac{1}{\omega}-\frac{2(2D)^{1/2}\langle c^2\rangle}{\omega^{3/2}\ln\dfrac{L_{\max}}{L_{\min}}}\cdot\frac{1}{L_{\max}}. \tag{5b}$$

In the frequency range

$$\frac{2D}{L_{\max}^2}<\omega<\frac{2D}{L_{\min}^2} \tag{6}$$

we can ignore the second and fourth terms on the right hand side of Eq. (5b). The noise spectrum reduces then to

$$G(\omega)=\frac{4\langle c^2\rangle}{\ln\left(\dfrac{L_{\max}}{L_{\min}}\right)}\cdot\frac{1}{\omega}.$$

Above the frequency corresponding to $L_{\min}$, we get $\omega^{-3/2}$ behavior, and below the frequency corresponding to $L_{\max}$ we get $\omega^{-1/2}$ an ω^{-1} spectrum.

As an example of the range of the f^{-1} noise, consider $D=1.5\times10^{-9}$ $\mathrm{m^2\,s^{-1}}$, $L_{\max}=10$ μm, giving $\omega=30$ or $f=5$ Hz as the lower limit for f^{-1} spectrum. For $L_{\min}=0.1$ μm, the upper limit is $\omega=3\times10^5$, or $f=50$ kHz. For $L_{\min}=1$ μm, the upper limit is $f=500$ Hz.

This calculation is not entirely conclusive, as it considers only one dimensional diffusion, and requires a mathematical approximation. It may be useful also to include a drift term, as well as diffusion. Furthermore, taking the length distribution $q(L)\propto 1/L$, although reasonable on the assumption that there are more ways to have short than long paths, nevertheless is somewhat arbitrary. However, given the universal $\omega^{-3/2}$ behavior of diffusion noise at high frequencies, the ω^0 to $\omega^{-1/2}$ behavior at low frequencies, and the fact that for path lengths of interest in many membrane systems the changeover comes in the range in which the spectra are measured, it is a strong indication that diffusion noise is a probable source of $1/f$ noise in at least some of these systems. The experimental results on the membranes of essentially fixed path length indicates that diffusion is indeed the principal noise source for transport through pores of that type of membrane. It would appear reasonable that this is the source in other cases where it is physically reasonable, and where $1/f$ noise is found.

It must be emphasized that diffusion is not the only source of $1/f$ noise. As mentioned above, van der Ziel (1950) and du Pre (1950) showed that a distribution of relaxation times produces $1/f$ noise over a finite region. Recently, Feher and Weissman (1975) showed a similar result with thermal fluctuations in an electrolytic solution specially chosen to maximize this effect. Furthermore, Handel (1971), Teitler and Osborne (1971), and Tchen (1973*a*, *b*) have shown that $1/f$ noise may result from the cascading of turbulent energy, a phenomenon which may be of biological significance.

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