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Excess Electrical Noise During Current Flow Through Porous Membranes Separating Ionic Solutions

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Summary. Spectral analysis of electrical noise from various artificial membrane systems suggests that excess noise of an f^{-n} spectral form, where n is approximately unity, is not primarily a bulk phenomenon simply dependent on the number of charge carriers. Measurements from aqueous and nonaqueous electrolytic resistors, comprised of several different ionic species, show only flat power density spectra under applied currents, even at extreme dilutions. Excess noise of f^{-n} form is observed under applied d-c current in single pore membranes, as previously reported, but is also seen in multipore and polymer mesh membranes. Calculations based on single pore membrane noise data are in significant variance with the bulk charge carrier model proposed by Hooge. These observations suggest that such excess noise occurs in conjunction with anisotropic constraints to ion flow.

Measurements of fluctuations in either membrane potential or current in three nerve membranes (Derksen & Verveen, 1966; Poussart, 1971; Fishman, 1972; Fishman, Moore & Poussart[1]) have shown noise 2–3 orders of magnitude in excess of the noise which can be accounted for from fluctuations of membrane resistance due to thermal agitation. The power density spectra, $S(f) = \overline{\Delta x^2}/\Delta f$, where $\overline{\Delta x^2}$ is the mean-square fluctuation in potential or current and Δf is the measurement bandwidth, have a strong component of the form f^{-n}, where n is approximately unity. In all of the neural membranes the $1/f$ noise appears to be related to potassium ion current flow.

Recent work (Fishman, 1973; Siebenga, Meyer & Verveen, 1973; Fishman *et al.*[1]) has shown an additional noise component of the Lorentzian

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[1] Fishman, H. M., Moore, L. E., Poussart, D. J. M. 1975. Potassium ion conduction noise in squid axon membrane. *J. Membrane Biol. (Submitted for publication)*.

form $[1+(f/f_c)^2]^{-1}$ which, in the case of the squid axon membrane, has been shown to relate to potassium channel conduction (Fishman, 1973, 1975; Fishman *et al.*[1]). These data, as well as computations of power spectra (Hill & Chen, 1972; Stevens, 1972) from the Hodgkin-Huxley (1952) formulation, strongly suggest that the fluctuations which produce Lorentzian spectra are associated with ion-channel conduction kinetics whereas the fluctuations which produce $1/f$ noise are not. What, then, is the phenomenon which produces $1/f$ noise and involves potassium ion flow in nerve membranes; and, could these data yield, in addition to the Lorentzian spectra, useful information about some aspect of potassium ion movement through membranes?

$1/f$ noises have been of great mystery for quite some time in solid-state matter (Watkins, 1959). McWhorter (1956) concluded that this noise is predominately, if not entirely, a surface phenomenon. This conclusion was based upon the evidence that the $1/f$ noise amplitude could be increased through surface treatment (Maple, Bess & Gebbie, 1955; Pearson, Montgomery & Feldman, 1956) and his rejection of the observation by Montgomery (1952) that $1/f$ noise may result from the change in lifetime of minority carriers. It had been known for some time (Bernamont, 1937) that by superposing shot noise spectra of the type $\tau/[1+(w\tau)^2]$ with a distribution function for the time constant τ, which is proportional to $1/\tau$, a $1/f$ spectrum can be obtained. McWhorter (1956) dismissed this possibility by arguing that the activation energy associated with processes giving rise to such a time constant would have to be much smaller than have actually been measured. Other models (Richardson, 1950; Bess, 1953; Schönfeld, 1955; *also* Clarke & Voss[2]; Voss & Clarke[3]) involving ionic diffusion processes have produced $1/f$ spectra over a wide frequency range, however. McWhorter rules some of these out as the basis for explaining all $1/f$ noise. He proposes a model for $1/f$ noise in a $p-n$ junction (McWhorter, 1956) which hypothesizes that at the surface region between the two materials, the majority carriers in each of the semi-conductors become trapped in surface states, and that the random trapping and emission of these carriers, which eventually recombine, produce the $1/f$ spectrum.

Clearly, we shall not provide answers to the questions posed above in this paper. Instead we present results of experiments which were conducted to test a proposal by Hooge and colleagues (Hooge, 1969; Hooge & Hoppen-

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[2] Clarke, J., Voss, R. F. 1974. $1/f$ noise from the diffusion of particles or heat. *Physics Letters (Submitted for publication).*

[3] Voss, R. F., Clarke, J. 1974. Fluctuation spectra for systems obeying a diffusion equation. *Physics Letters (Submitted for publication).*

brouwers, 1969*a*, *b*, *c*; Hooge, van Dijk & Hoppenbrouwers, 1970; Hooge & Gaal, 1971) which, in contrast to surface phenomenon models, suggests that 1/*f* noise can occur in bulk conductors from the fluctuations in mobilities of charge carriers, which in turn produce conductance fluctuations. This particular proposal is of interest since it would provide the basis for calculation of K^+ membrane mobilities from existing noise data in three axons.

Our studies progressed from noise in nonaqueous ionic solutions to simple holes in sheets of nonconducting materials (Mylar and mica) to, the not so simple, micromeshes in two polymeric membranes (collodion and Formvar). The results from these systems show significant variance from the proposal by Hooge.

Materials and Methods

Fig. 1 illustrates the instrumentation and experimental chamber for measurement of noise and its spectral analysis in membranes. Membranes were cemented between two Plexiglas or glass plates with apertures of about 0.5 cm in diameter and clamped between two chamber halves in an aluminum vise. Two Ag/AgCl spiral electrodes were used to pass current and two Ag/AgCl spirals were used to measure the voltage fluctuations (Fig. 1). Experiments were also conducted on electrolyte-filled micropipettes (De Felice & Firth, 1971). The two Ag/AgCl electrodes in either side of the capillary tip were used to pass current and to record noise voltage simultaneously.

Current-voltage plots were made for all membranes investigated to ensure linearity within range of voltages applied during noise measurements. The noise characteristics of the preamplifier (Princeton Applied Research PAR 113), with known input resistance terminations used as thermal noise sources, has been reported (Fishman & Dorset, 1973).

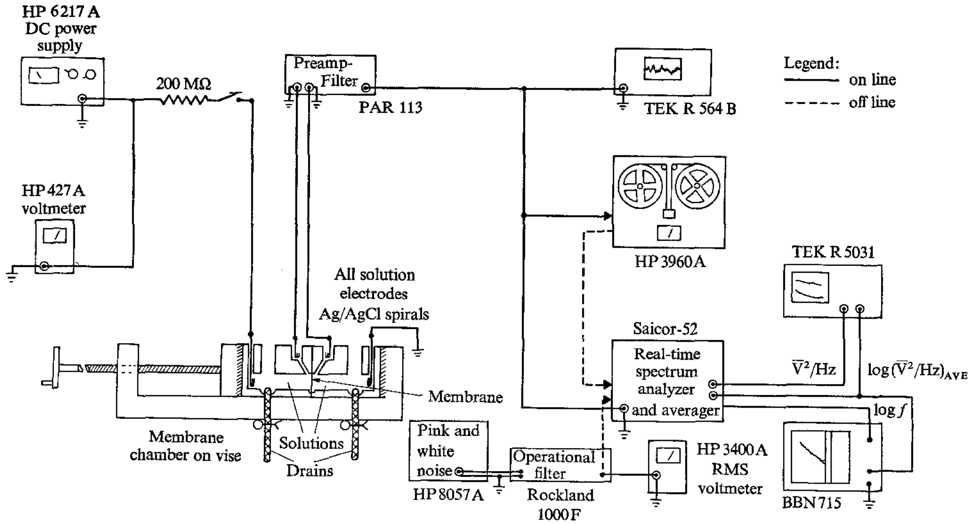

Fig. 1. Scheme of noise measurement and analysis system

The useful operating impedance level is between 100 kΩ and 10 MΩ because of the intrinsic amplifier noise and its input capacitance, which limit the observation of low and high frequency noise components, respectively. Other workers have avoided preamplifier high frequency effect with high source impedances by using negative capacitance amplifiers (Derksen, 1965), but we avoided this method because of the noise contributions due to the feedback system which must be used. In the experimental set-up outlined in Fig. 1, amplification and filtering were available from a Rockland 1000 F operational filter which could be inserted between the PAR 113 output and the analyzer input. With a PAR 113 voltage gain of 10^3 or greater, the operational filter contribution to the total noise was negligible.

The Fourier components of the amplified noise signal were analyzed with a 400-line Honeywell-Saicor 52 real-time spectrum analyzer and averager (Fishman *et al.*[1]). This analyzer allows preselection of the frequency bandwidth and the number of independent real-time spectra to be summed and averaged (for statistical accuracy). In connection with spectral measurement with this instrument, since there is no present precise definition for $1/f$ noise, we have followed the lead of Bennett (1960) in accepting a range of spectral slopes from 0.30 to 1.5 as falling in this noise category. Previously reported measurements have consisted of a relatively few number of points and thus the determination of $1/f$ slopes may have suffered in accuracy due to other undiscernable noise components. A Hewlett Packard 8057 A noise generator and the operational filter were used for calibration and generation of known spectra (Fishman *et al.*[1]). Repetitive analyses of a given noise signal with this system are very precise, both with respect to shape of spectral envelope and power density levels.

The experimental chamber and amplifier were placed in a Faraday cage to minimize "60-cycle" line interference and its harmonics. Even though these components could not be observed in the time series signal, spectral analysis often showed these components as discrete "spikes" in the power spectra. Because these components do not interfere with the slope of the spectrum, they have been eliminated from all spectra presented in this paper except one. Fig. 3, an overlay of three separate analysis bands, illustrates that 60-Hz and related spectral components can be readily distinguished from the noise of the experiment. Vibrational perturbations to the membrane chamber were damped by shock mounting the membrane chamber and noise preamplifier (PAR 113).

Solutions

Aqueous salt solutions were prepared from J. T. Baker analyzed reagents in glass-distilled water which had been passed through a train of ion exchange columns and Millipore filters. Reagent grade organic solvents (J. T. Baker Co. and Eastman Organic) were used from the bottle except for nitrobenzene which was twice vacuum distilled.

Micropipettes

Glass pipettes were drawn on a vertical pipette puller to give tip diameters ≦ 1 µm. These pipettes were drawn from either Kimble N 15 a "Kimax" glass capillaries (OD 0.6–1.0 mm) or Corning 9530 "Pyrex" glass capillaries (OD 1.5 mm) and filled with a 3.0 M KCl solution.

Polyethylene terephthalate ("Mylar") Film

Mylar film 25 µm thick was obtained from a reel of Scotch 900-1-400 IR one-inch magnetic tape and 12.5 µm thick film was taken from a reel of Scotch 144-1/4-1200 quater-inch magnetic tape. Single holes ≦ 25 µm were punched with fine-tipped needles. Pore sizes were estimated with a microscope having a calibrated reticule.

Collodion Film

Collodion films were cast from 4% collodion in ether/alcohol solution (J. T. Baker Co.) according to Blinks' (1930) procedure. An observation of the interference colors seen as the films floated on a water surface (Peachey, 1958) gave a thickness estimate of about 2000 Å.

Polyvinyl Formal ("Formvar") Film

Formvar films were prepared by dipping a clean glass slide into a 2% chloroform solution of the polymer and floating the dried films off onto a clean distilled water surface. Interference colors of the floating films gave a thickness estimate of 2000 Å (Peachey, 1958; Rauth, 1962).

Etched Mica Sheets

Approximately 5 μm thick mica sheets were cleaved from clear ruby Muscovite (Essex International Inc., Peabody, Mass.). The thicknesses were determined using dimensions of the weighed sample and an assumed density of 2.8_4 g/cc (Bean, Doyle & Entine, 1970). Fission tracks from natural uranium impurities were etched with hydrofluoric acid (Price & Walker, 1962; Bean *et al.*, 1970). Large pore sizes were observed directly with a Zeiss interference microscope.

Results

Electrolyte Solutions

Control experiments were carried out with various electrolytic resistors composed of solutions of NaCl, NaBr and KCl (concentration range: 0.1 to 1.0 M) in glycerol as well as solutions of LiCl (concentration range 0.1 to 1.0 M) in glycerol, propylene glycol, 1-propanol and *n*-pentanol. These solutions were placed in 8 mm diameter tubes about 75 cm long with two Ag/AgCl spirals at each end. A constant d-c current source was used to apply steady-state potentials up to 100 mV to the Ag/AgCl electrodes from which the noise voltage was measured simultaneously. Typical flat power spectra in Fig. 2 demonstrate that variations in solvent polarity, viscosity and number of functional groups (in the solvent molecule) as well as variations in ion mobility do not in themselves alter the "white" noise character of electrolytic resistors (Johnson, 1928) in the measured frequency band. Similar measurements were made with Ag/AgCl electrodes in dilute aqueous KCl solutions down to 10^{-5} M as a control for later experiments with membranes bathed with such solutions. In all cases the noise was "white".

In an attempt to lower the number of charge carriers in a bulk medium, twice fractionally vacuum distilled nitrobenzene, which was afterwards washed with conductivity water, was equilibrated with aqueous 1.5×10^{-5} M KCl. Using Davies' (1950) value for the KCl distribution co-efficient

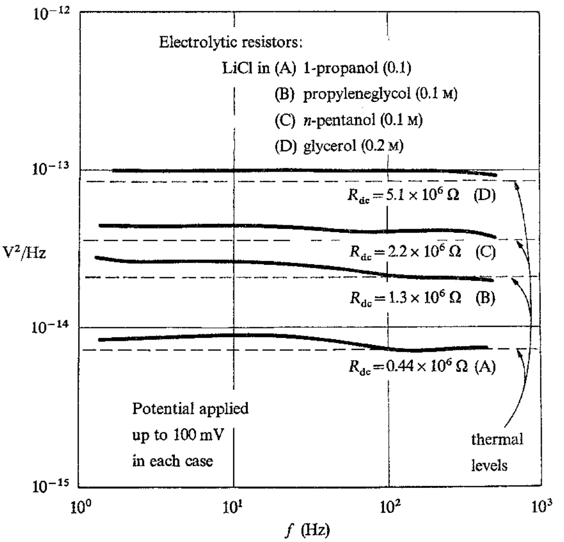

Fig. 2. Power density spectra for noise from electrolytic resistors. R_{dc} is the measured resistance of the electrolytic resistors. Dashed lines indicate thermal noise level calculated using R_{dc} in the Nyquist (1928) equation

between nitrobenzene and water $B_{w/o} = 2.3 \times 10^5$, and assuming the presence of no ionic contaminants, a KCl concentration of 6.5×10^{-11} M in nitrobenzene is calculated. All glassware was cleaned with $Na_2Cr_2O_7 - H_2SO_4$ cleaning solution, rinsed 5 times with tap water, then rinsed 5 times with conductivity water and ovendried. Independent measurements of resistivities at 400 Hz in a calibrated conductivity cell with platinum spiral electrodes gave no measurable change in resistivity ($\rho = 26 \times 10^6\ \Omega$ cm at 25 °C) when the nitrobenzene was equilibrated with the dilute KCl solution. A measureable change in resistivity ($\rho = 6 \times 10^6\ \Omega$ cm) when nitrobenzene was equilibrated with 1 M KCl allowed a calculation of the apparent charge carrier mobility in this solvent $\mu = 2 \times 10^{-4}$ cm^2/V sec.

Upon application of ± 0.80 V to the nitrobenzene system across two parallel platinized silver plates (3.0 cm × 2.7 cm) spaced 0.2 cm apart, no discernable deviation from white noise was observed over the frequency range, 1–10^3 Hz. A similar experiment with pure ethyl benzoate between the electrode plates ($\rho = 3.0 \times 10^9\ \Omega$ cm) also gave no indication of excess noise when current was passed through the medium.

Micropipettes

Fig. 3 shows power spectra from a Pyrex microtip filled with and dipping into aqueous 3 M KCl. At zero applied potential, the white noise level is

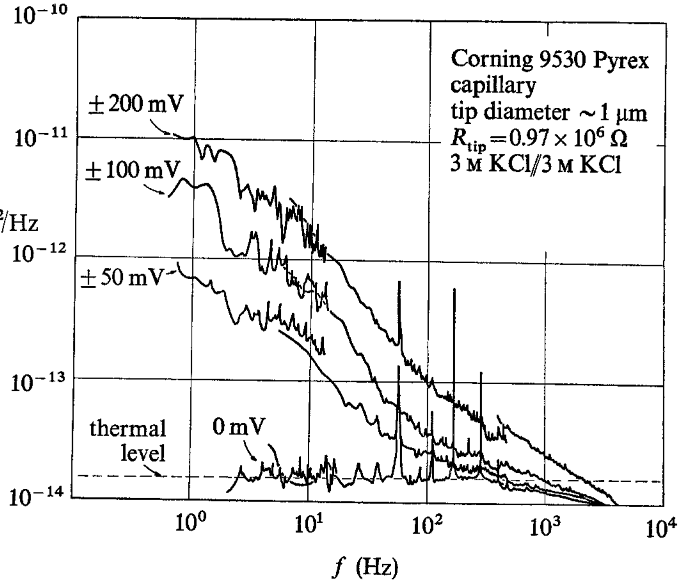

Fig. 3. Noise from Pyrex microtip. Overlap of three separate analysis bands shown. Also note spiking due to "60 cycle" line interference

commensurate with the value predicted by the Nyquist (1928) equation for a resistor of the same tip resistance as the micropipette ($R_{dc} = 0.97 \times 10^6\ \Omega$). There was a measured tip potential of 4 mV.

Low frequency noise components, in excess of thermal levels, with f^{-n} declines where $n \simeq 1$ (*see* Table 1)[4], occur in the power spectra at applied d-c potentials. The approximately $1/f$ spectral shape is in apparent agreement with the limited data of DeFelice and Firth (1971) which consist of only a few spectral points, determined at relatively large bandwidths. Similar results were observed across a Kimax glass micropipette. Power densities of the noise levels at 1 Hz are given in Table 1 for two micropipettes at several applied d-c potentials.

Polyethylene terephthalate ("Mylar") Films

A representative power density spectrum for nonequilibrium noise across a single pore in a thin Mylar sheet separating two aqueous KCl

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[4] The slopes of power spectra were determined from straight lines fit by eye to the continuous spectra. There was no subtraction of thermal noise from the excess noise spectra, because of the assumption that white noise and excess noise are uncorrelated. Since the excess noise in all cases is significantly greater in magnitude than the thermal noise, the thermal noise component should not disturb the accuracy of the measurement significantly. Deviation from unit slopes in the excess noise spectra may indicate other noise components such as $1/f^2$ (e.g., *see* Fig. 6).

Table 1. Calculations of α in Hooge equation from micropipette data

Tip diameter (cm)	Glass	d-c resistance (Ω)	KCl conc. (M)	Spectral slope (−n)	Applied potential (V)	xs noise at 1 Hz (V^2/Hz)	α
$\simeq 10^{-4}$	Pyrex	0.97×10^{6}	3.0	0.96	±0.20	1.0×10^{-11}	140
				1.0	±0.10	4.0×10^{-12}	230
				0.74	±0.050	7.0×10^{-13}	160
$\simeq 0.5\times10^{-4}$	Kimax	2.4×10^{7}	3.0	0.96	±0.10	9.0×10^{-11}	640
				0.98	±0.050	7.0×10^{-11}	2000
				0.83	±0.020	$1.3+10^{-11}$	2300

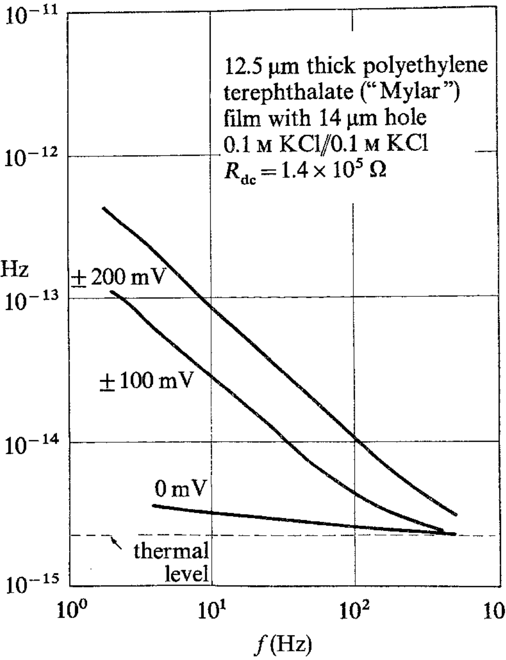

Fig. 4. Noise from Mylar film with single 14 μm hole

solutions is given in Fig. 4. Again the approximately f^{-1} falloff appears only for applied potentials – in agreement with the observation of Hooge and Gaal (1971)[5]. In some cases the power spectra were more curved

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[5] A difference between our experiments with Mylar and those of Hooge and Gaal is that we only used aqueous KCl solutions and Ag/AgCl electrodes, whereas Hooge and Gaal used several metal salt solutions in contact with the corresponding metal electrodes. Our own experience with such metal/metal salt systems, in particular when the metal ion is divalent, is that significant excess noise can be present at applied voltage even at appreciable salt concentrations. Monovalent ionic solutions in contact with the parent metal electrodes however only gave white noise under applied voltage. As indicated above, the Ag/AgCl/KCl (aq)/AgCl/Ag system alone also only gave white noise under applied voltages.

Table 2. Calculation of α in Hooge equation from Mylar noise data

Film thick-ness (μm)	Obs. pore diam. (μm)	KCl conc. (M)	$R_{dc}(\Omega)$ meas	$R_{dc}(\Omega)$ calc	Applied poten-tial (V)	*xs* noise at 1 Hz (V^2/Hz)	Spectral slope ($-n$)	α
25	28	0.01	9.2×10^6	2.2×10^5	0.50	1.5×10^{-10}	1.20 → 1.51	320
					0.40	5.0×10^{-11}	1.18 → 1.38	170
					0.35	2.0×10^{-11}	1.05 → 1.38	95
					0.30	5.0×10^{-12}	1.10	30
					±0.20	3.4×10^{-12}	1.20	45
					0.10	1.5×10^{-13}	0	8.0
12.5	28	0.01	5.7×10^5	4.3×10^5	±0.50	1.0×10^{-12}	0.87	2.1
					±0.20	1.2×10^{-13}	0.56	1.6
					±0.10	3.8×10^{-14}	0.29	2.0
12.5	14	0.10	1.4×10^5	1.2×10^5	±0.20	7.0×10^{-13}	0.93	12
					±0.10	2.0×10^{-13}	0.83	13
12.5	14	0.10	0.59×10^5	1.2×10^5	±0.50	2.8×10^{-13}	0.83	0.37
					±0.20	6.9×10^{-14}	0.68	0.23
12.5	14	0.10	1.7×10^5	1.2×10^5	±0.50	1.4×10^{-13}	0.76	0.19
					±0.20	5.2×10^{-14}	0.78	0.17
					±0.10	1.8×10^{-14}	0.59	0.12
12.5	5	0.10	0.69×10^6	0.64×10^6	±0.50	1.1×10^{-11}	0.98 → 1.41	0.22
					±0.20	0.87×10^{-12}	0.62 → 1.05	0.04
					±0.10	2.5×10^{-13}	0.50 → 0.80	0.03

(convex side downward) than linear. Thus, in the listing of noise levels at 1 Hz for several membranes given in Table 2, the maximum and minimum slopes of the tangents of curved spectra are listed.

A manifestation of the extreme nonwettability of Mylar surfaces (Ellison & Zisman, 1954) was the long "filling time" for pores through these sheets. As much as a day's standing was required to obtain a resistance close to the spreading resistance predicted for a cylindrical channel and accounts for difference in measured resistance (Hooge & Gaal, 1971);

$$R=\rho\left(\frac{1}{2a}+\frac{t}{\pi a^2}\right) \tag{1}$$

where a is the pore radius, t is the membrane thickness and ρ is the resistivity of the surrounding aqueous medium. Numerical values for the latter are found in the *Handbook of Chemistry and Physics* for various concentrations of KCl. A comparison of measured and calculated resistance also appears in Table 2 for each membrane.

Mica Sheets

Since large pores in HF-etched Muscovite were also found to give nonequilibrium excess noise with nearly a f^{-1} decline. Although single large

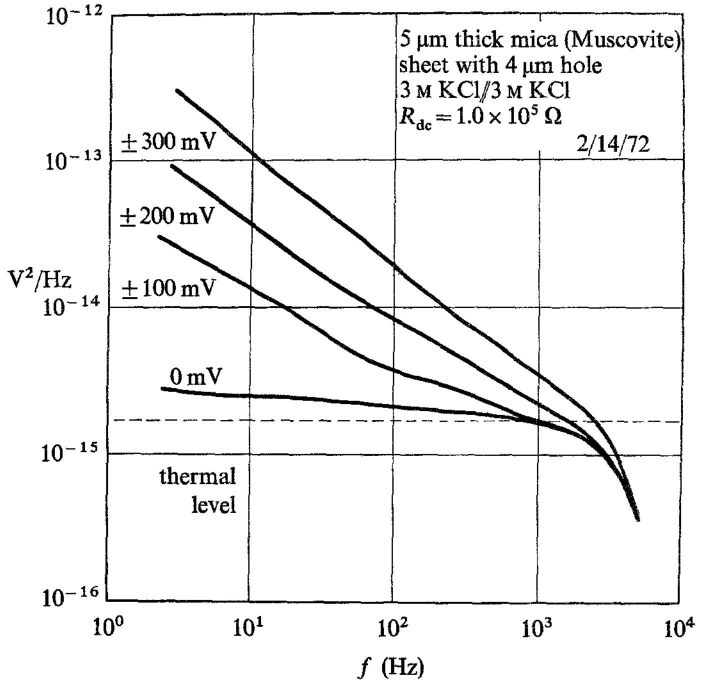

Fig. 5a

Fig. 5. Noise from 5 μm thick mica sheet with single 4 μm hole on two consecutive days. The sharp high frequency rolloff is due to the playback filter characteristics of the FM tape recorder. Note that the possible presence of unseen micropores adjacent to the large isolated pore cannot be discounted

pores were isolated on a mica sheet by melting wax on the surface surrounding a pore, the presence of additional adjacent uncovered micropores which are unobservable in the (light) interference microscope cannot be discounted. Two representative sets of spectra for a single membrane are shown in Fig. 5*a* and *b*, which show that the apparent noise power for a given applied potential and a given solution concentration is not necessarily constant. Mica data are given in Table 3. In one membrane, slight rectification across the holes was measured. Accordingly, the greater excess noise was observed in the direction of greater resistance.

Another noise measurement was made with a mica sheet which had been etched for 5 min in 50% HF. Here, unlike the above experiments which used isolated large pores, a membrane with multiple small pores (≃ 1000 Å) was used. The set of power density spectra were similar to those from the large pore membrane except for departure from linearity at low frequency. (There is, however, no stretch of the envelope where another

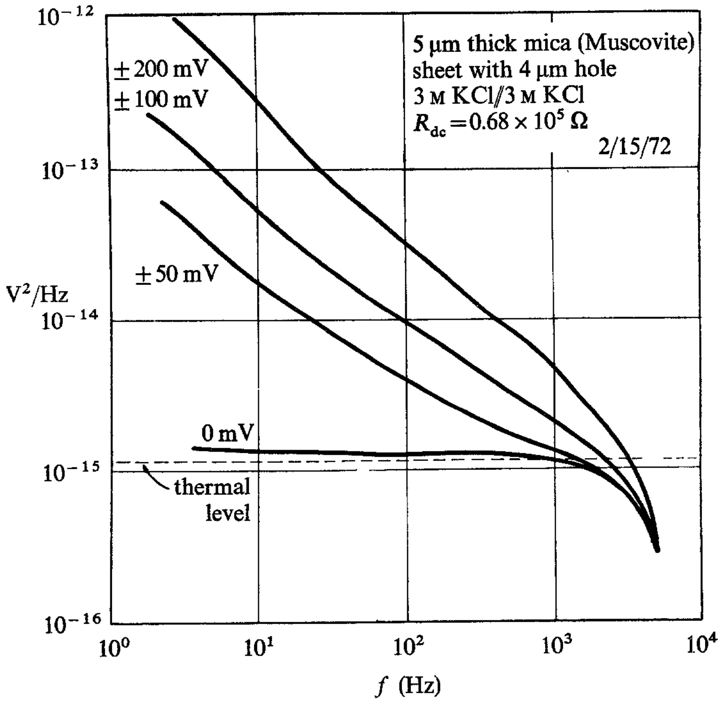

Fig. 5b

Table 3. Calculation of α in Hooge equation from mica data

Film thickness (μm)	Obs. pore diam. (μm)	KCl conc. (M)	R_{dc}(Ω) meas	Applied potential (V)	*xs* noise at 1 Hz (V^2/Hz)	Spectral slope ($-n$)	α
5	2	3.0	0.92×10^6	0.30	8.0×10^{-11}	1.0	52
			0.65×10^6	−0.30	1.2×10^{-11}	1.0	8.0
				0.20	2.5×10^{-11}	1.0	36
				0.20	4.0×10^{-12}	0.98	6.0
				0.10	6.0×10^{-12}	1.0	35
				−0.10	2.0×10^{-12}	1.0	12
				0.05	8.0×10^{-13}	0.67	19
				−0.05	4.5×10^{-13}	0.75	10
5	4	3.0	1.0×10^5	±0.30	7.0×10^{-13}	0.78	3.6
				±0.20	1.7×10^{-13}	0.65	2.0
				±0.10	4.5×10^{-13}	0.55	2.1
5	4	3.0	0.68×10^5	±0.20	2.5×10^{-12}	0.90	29
				±0.10	3.8×10^{-13}	0.75	18
				±0.05	1.2×10^{-13}	0.73	22

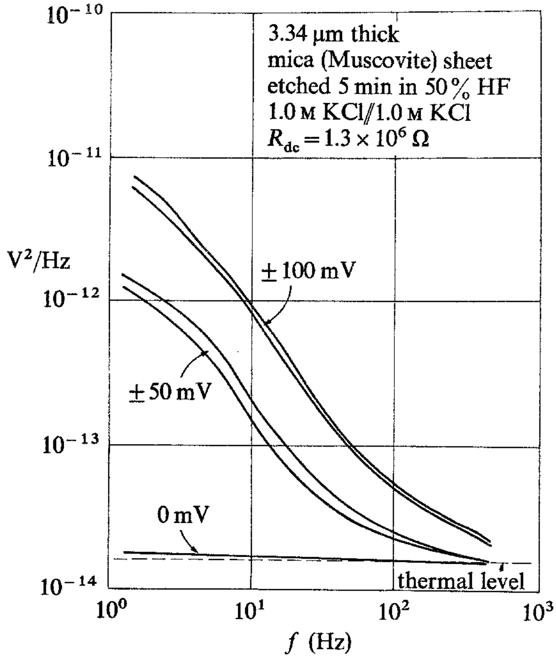

Fig. 6. Noise from mica sheet etched in 50% HF to give multiporous membrane

discrete noise component can be unfolded from the predominately $1/f$ falloff.) These data are represented in Fig. 6. The spectra at ± 100 mV and ± 50 mV applied potential, respectively, fall off as − 1.38 and − 1.23 powers of f.

Collodion Films

Collodion, a polymer film with mean "pore" sizes of about 1000 Å (Elford, 1930), behaves like the previously discussed membranes under applied constant current. A representative experiment is summarized in Fig. 7. The power density spectra have slopes between − 0.87 and − 0.96 in this experiment. Similar results from collodion-impregnated filter papers were obtained by DeFelice and Michalides (1972).

Polyvinyl Formal ("Formvar") Films

Formvar films have been estimated to have a mesh ranging from 40 to 1000 Å (Plavnik, Sinitsyna & Vlodavets, 1966). Representative power spectra of nonequilibrium noise across thin Formvar films are shown in Fig. 8. Slopes ranging between − 0.36 and − 1.18 have been determined from the data of several Formvar films examined. In Fig. 8 the slopes range from − 0.71 to − 1.0.

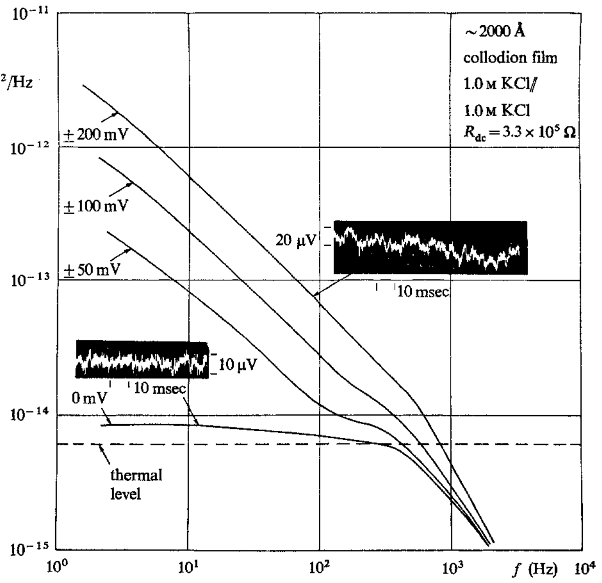

Fig. 7. Noise from collodion film. Note difference in appearance of time sequence signals from thermal and excess noise

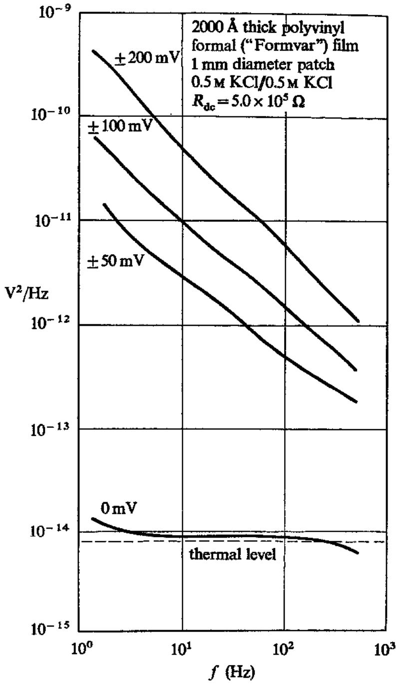

Fig. 8. Noise from polyvinyl formal film

Discussion

The results presented in this communication and in papers by other workers (DeFelice & Firth, 1971; Hooge & Gaal, 1971; DeFelice & Michalides, 1972; Michalides, Wallaart & DeFelice, 1973) demonstrate that excess noise of the f^{-1} type occurs in simple porous films and polymeric membranes. In order to determine whether the observed noises in porous membranes may be useful in describing ion movement noises in cell membranes, a physical explanation of the source of noise in these simple systems is required.

Our data indicate that $1/f$ or noise other than white is not an observable phenomenon in simple electrolytic resistors where various solvent and solute physical parameters are varied. This has been recently confirmed by other workers (Vasilescu, Teboul, Kranck & Gutmann, 1974). The only reported observation of nonwhite excess noise in an electrolytic system was in a solution of an electrolyte ($BeSO_4$) in equilibrium with its precipitate under applied electrical field (Feher, 1970; Feher & Weissman, 1973). The form of the spectral envelope is Lorentzian.

As indicated in the introduction, in a recent explanation of $1/f$ noise, it was proposed that fluctuations of this type arise from the bulk property of solutions. Hooge and his co-workers have formulated an empirical equation based on their experimental data where the noise power, $\overline{\Delta x^2}$, is directly proportional to the square of the applied d-c potential and inversely proportional to the number of actual charge carriers N in the system, *viz.*:

$$\overline{\Delta x^2} = \overline{x^2} \frac{\alpha}{N} \frac{\Delta f}{f}. \tag{2}$$

Here x can be either resistance or voltage and α is a constant with a value of 2×10^{-3} for electrons and for holes in solid state materials (Hooge, 1970) and a value some 10^4 higher for molar concentrations of ions in solution (Hooge & Gaal, 1971). The parameter Δf is the bandwidth and f is the frequency.

The most logical test of this bulk hypothesis and Eq. (2) would be to measure the noise from extremely dilute solutions of ions. Since noise other than thermal was not observed from such electrolyte solutions, it appears that Eq. (2) does not apply to bulk solutions. However, there is the possibility that the excess noise predicted by Eq. (2) was below the thermal noise level of the solutions. The range of α for which Eq. (2) is not applicable can be estimated from the nitrobenzene data.

The minimum noise above thermal (2.3×10^{-14} V^2/Hz) which the analysis system could detect (error 25%) is 0.58×10^{-14} V^2/Hz. From Eq. (2), this would require $\alpha < 1.1 \times 10^{-3}$ for a noise measurement at 1 Hz with a 1 Hz bandwidth and an applied voltage of 0.80 V to 1.6 cm^3 of 6.5×10^{-11} M KCl in nitrobenzene. This value of α neither agrees with the value for 1.0 M ions (10) nor with that for electrons (2×10^{-3}) cited by Hooge (1969) and Hooge and Hoppenbrouwers (1969*a*, *b*, *c*). The dependence of the constant α on ion concentration suggested later by Hooge and Gaal (1971) would place $\alpha \simeq 10^{-9}$ for *ca.* 10^{-10} M KCl (a value much lower than that given by them for electrons) if the relationship is linear. However, their own experimental observations only cover a 100-fold range of concentration with a lower limit of 5×10^{-2} M and give no indication of what should be expected at extreme dilution. Since no change in resistivity was measured upon equilibration of nitrobenzene with aqueous 1.5×10^{-5} M KCl, it also remains uncertain what charged species is actually carrying the current. Charged nitrobenzene molecules stabilized by the molecular π-system and formed at the electrodes could be an important contribution to the total charge carrier flows, as has been suggested by studies on other pure solvent systems (Gzowski & Terlecki, 1959; Le Blanc, 1959; Adamczewski & Jachym, 1966). Preliminary experiments with pure nitrobenzene and with ethyl benzoate in our laboratory have been frustrated, however, by the requirement of a stable noise-free current source and a severe sensitivity to vibrations as a consequence of the high impedance of these solvents.

Another test of Eq. (2) is to compute values of α from the data for single-pore membranes given in the Tables and to compare these with those predicted by Hooge and Gaal (1971). For microtips, an expression derived by K. S. Cole from the spreading resistance of a hole of such geometry gives for N in Eq. (2):

$$N = \frac{5\pi n d^3}{m}$$

where n is the number of ions/cc, m is the tangent of the angle of the pipette tip taper (usually about 0.1) and d is the tip diameter. Calculated values of α using this expression in Eq. (2) are given in Table 1 along with other data for micropipette noise. Hooge and Gaal (1971, Fig. 6) predict an α between 8 and 120 for a bi-ionic salt concentration of 3 M. Both sets of calculated α's in Table 1 are higher than predicted.

The expression for N in Eq. (2) derived from a point contact between two solutions is given by Hooge and Gaal (1971):

$$N = \frac{160 n a^3}{\pi^2}$$

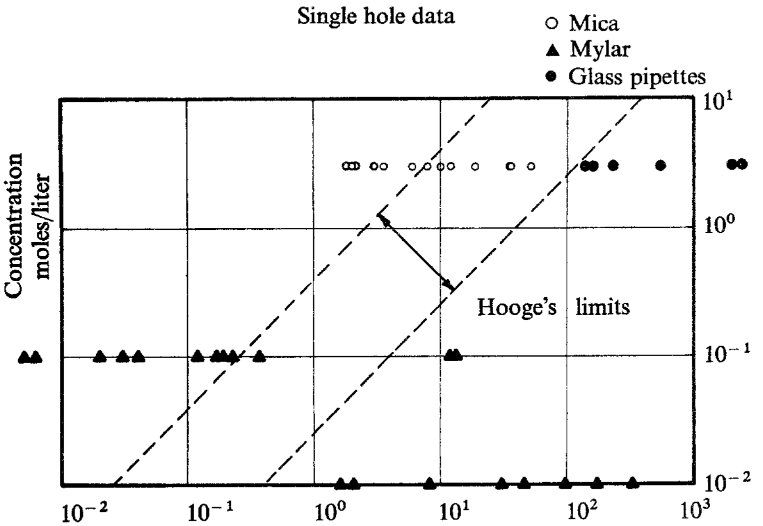

Fig. 9. Review of α values calculated with Eq. (2) for single pore membranes compared to limits specified by Hooge

and may be used to compare their predicted values of α with those calculated from the Mylar and mica noise data (given in Tables 2 and 3). In the above expression, n is again the number of ions/cc and a is the pore radius. Hooge and Gaal (1971, Fig. 6) predict an α-range of 0.025 to 0.40 for a salt concentration of 0.01 M and a range of 0.25 to 4.0 for a concentration of 0.1 M. As Tables 2 and 3 illustrate, even when the hole resistance agrees with the expected value (indicating a filled pore), there are generally significant deviations from the predicted value of α. The above data, summarized in Fig. 9, then indicate some mechanism other than a dependence on charge carrier concentration only.

In addition to suggesting that $1/f$ noise is not solely dependent on the number of charge carriers, these data also indicate that this noise is not particularly dependent on the type of material used as a porous membrane. Excess noise was observed in "membranes" made of two kinds of glass capillary, as well as in mica, cellulose, Formvar and Mylar. The silicates glass and mica would be expected to be polar (Radoslovich, 1960; Eisenman, 1966), cellulose and Formvar would be expected to hydrogen bond to water (Sollner, Abrams & Carr, 1940; Billmeyer, 1966), whereas Mylar is known to present a very nonpolar surface (Ellison & Zisman, 1954). The membrane geometry can be either one large pore or a network of small pores or a polymer mesh. In addition to material properties, all the holes or multipores examined are too large (1–30 μm diameter) to interfere with ion flow on an atomic scale either by adsorption of the ions themselves or by localized structuring of the solvent. Significantly, excess noise is absent from simple bulk flow systems. It thus appears that the observed excess noise is associated with the constraint to the bulk mass transport through the pores concomitant with d-c current flow.

In quest for a suitable explanation, another model for $1/f$ noise, also described as a bulk phenomenon, attributes this fluctuation event to a "hydromagnetic turbulence" resulting from instabilities of: (a) surface potential barrier, (b) the self-magnetic field of a current in the presence of a potential barrier transverse to the current flow direction, and (c) "recombination waves" (Handel, 1968*a, b*; 1971). While this theory has been formulated mainly for solid state systems, it seems an interesting prospect to test in future probes into the etiology of this fluctuation phenomenon from membranes separating ionic solutions.

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