

Flicker Noise of Ion-Selective Membranes and Turbulent Convection in the Depleted Layer

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Abstract. Flicker noise of electric currents through ion-selective membranes is explained. It is attributed to the depletion of salt on one side of the membrane, which creates a thin layer of high resistance. Joule heating in this depletion layer and the ensuing temperature gradient, as well as the concentration gradient, give rise to buoyant forces which may create a turbulent convection current. The turbulence mixes the depletion layer so that the electric resistance fluctuates, and consequently the current flickers.

Experiments with ion-selective membranes support this conjecture. They show that 1) Noise is coincident with the increase of the electric resistance by the depletion process. 2) When the current density is reduced, it reaches a critical value, below which the convection current changes from turbulent to laminar, and the noise disappears. 3) Noise reduces with temperature, because the expansion coefficient of water decreases with temperature, and its viscosity increases. 4) A non-ionic water-soluble polymer added to the compartment on the side of the depletion layer reduces the noise, by increasing the bulk viscosity of the solution. 5) Noise depends on the membrane's orientation in the gravitational field. 6) The convection-current in the depletion layer can be observed directly, using a laser-beam, by adding latex particles which create optical noise as they drift with the convection current across the beam. The optical noise is observed only coincidentally with the current noise.

Key words: Noise — Membranes — Ion selectivity — Convection — Turbulence.

Introduction

When an electric current passes through a certain class of membranes, a current noise is observed, which does not resemble either thermal or shot noise. This phenomenon was reported, to the best of our knowledge, first by Forgacs [11], and

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independently by Verveen and Derksen [22], and was studied extensively in both biological [2, 4, 5, 8, 10, 17, 18, 24] and synthesis membranes [7, 9, 12, 13, 15, 19, 25]. Such noise is commonly known as "flicker noise", or " $1/f$ noise". Membranes exhibiting flicker noise were often known or shown to possess ion-selectivity. Various mechanisms were suggested for the generation of noise [23]. However, it had been pointed out [5, 15] that the source or mechanism by which the flicker noise is generated was not well understood, and the subject was considered as "enigmatic" [23].

Here we suggest a mechanism for the generation of noise in membranes, and report on a series of experiments on low-resistance ion-selective membranes, designed to examine the validity of our suggestion on such membranes. The results of these experiments prove the existence of the suggested mechanism in the ion-selective membranes. They also indicate the possibility to extend these considerations and experiments, in order to determine whether a similar mechanism applies to other types of membranes, including high-resistance porous membranes, synthetic as well as biological.

The outlines of the present theory and its predicted consequences are as follows.

It is well known that when a direct electric current passes through an ion-selective membrane, the solution is depleted of salt in the adjacent layer on one side of the membrane and is enriched on the other side [14]. The density of the electrolyte solution decreases in the depleted layer and increases in the enriched layer. This creates a buoyant force in the gravitational field, which drives the liquid of the depleted layer upwards, and that of the enriched layer downward. The upward motion of the liquid in the depleted layer is further enhanced by the big increase of the electric resistance in the depleted layer, which causes local Joule heating by the current [1]. The ensuing rise of temperature takes place mainly in that part of the depletion layer which is immediately near the membrane, where depletion and therefore resistance is the highest. The thinner the high resistance layer, the smaller its heat capacity, and therefore the larger its rise of temperature. The temperature gradient also creates, by the thermal expansion of water, a density gradient. Thus two density gradients are formed in the depletion layer, one due to the reduced concentration and the other due to the raised temperature. These gradients may set up hydrodynamic convection currents driven by the gravitational buoyant forces in the depleted layer. At sufficiently large gradients, the convection currents become turbulent. Turbulent currents mix the solution irregularly within and around the depleted layer, thus causing fluctuations in the electric resistance of the depleted layer. These resistance-fluctuations are observed as flicker noise. Note that the convection current in the enriched layer does not contribute to the flicker noise, because the rise of the electrolyte concentration in the enriched layer does not affect the resistance of the cell.

According to the present theory, the power spectrum of the current noise should be related to the spectral properties of turbulent convection [3, 16, 21]. Indeed, both are known to occur in the low frequency range. However, their spectral analysis requires a separate study, and will not be dealt with here.

Much may be learned, however, about the effect of buoyancy and hydrodynamic turbulence on flicker noise by performing a number of experiments to test some of the predictions of the present theory which are neither dependent on, nor

related to the power spectrum of flicker noise. The results of such experiments are reported here in the Results Section. They all confirm the main outlines of the theory, and raise a number of questions which will be brought up in the Discussion Section.

Two of the observable consequences of our theory have been already reported by Green and coworkers [13; 19], although without relating them to the turbulent convection in the depleted layer by the gravitational forces¹. These are:

1) The onset of noise must be preceded by the formation of the depleted layer, as the cause of hydrodynamic instability. Indeed Green and Yafuso [13] observed the coincident onset of both the rise of voltage across the membrane at constant current and the voltage noise. They rightly concluded that "this strongly suggests that cation exchange noise is intimately related to the formation of a depletion layer". Our experiments, performed at constant voltage, confirm and complement their result.

2) At sufficiently low current densities, the convection current should be laminar, therefore the electric current should be noiseless. Since the transition between laminar and turbulent flow is discontinuous, the onset of noise with increasing current density should also occur discontinuously at a critical current density. Such a transition was observed by Green and Yafuso [13] as well as by us. A similar distinction between weak and strong current was made by Block and Kitchener [1] in their study of polarization effects in ion-exchange membranes.

Other observable consequences predicted by the theory are:

3) The noise must decrease with temperature, because convection should be reduced by decreasing thermal expansion of water and by increasing its viscosity.

4) The noise should be damped by increasing the bulk viscosity of the depleted layer, say by adding a non-ionic water soluble polymer, while leaving ionic mobility and other relevant parameters unchanged.

5) When the selective membrane is kept in a horizontal position, the noise should depend on the direction of the current, being reduced when the depletion occurs below the membrane.

6) Membrane noise and turbulent convection should be found to set on simultaneously, when the convection is observed independently.

All the experiments described below were made on commercial membranes of high specific conductance and of diameter and thickness larger than the thickness of the depletion layer. Therefore they do not, strictly speaking, indicate whether the noise generated in other types of membranes, such as porous, high resistance biological membranes, has a similar mechanism. It is, however, interesting to enquire whether temperature gradients and buoyant turbulence may perhaps occur on a microscopic scale when an electric current flows through narrow channels of high conductance, whether ion-selective or not, in an otherwise high-resistance membrane.

¹ Stern and Green [18] suggest turbulence as one of three processes which dominate the noise power spectrum. However, they rejected the possibility that the gravitational turbulence observed by Block and Kitchener [1] was the source of noise. Instead they argued by analogy with Tchen's theory on plasma turbulence [20], that "the process is a production of turbulence due to drift in an unstable region, one in which a driving force (electric field, for instance) goes in the opposite direction to the concentration gradient". This suggestion requires either a more rigorous proof or an experimental evidence

Materials and Methods

The Conduction Cell

The conduction cell (Fig. 1) was made of two compartments, about 200 ml each, connected through two conical holes of 1.13 mm^2 in area. A semi-permeable membrane was inserted between the holes. The electrodes were of Ag-AgCl, prepared by standard methods. Their contribution to the current noise was examined and was found to be totally negligible. The ohmic resistance of the compartments (without the membrane), was $22.9 \text{ k}\Omega$ at 0.01 N KCl , most of it being contributed by the narrow holes near the membrane. All experiments were made with 0.01 N KCl water solutions at room temperature, unless specified otherwise.

Two cation-exchange membranes were used, with the following specifications: 1) The Selemion membrane²; ion-exchange capacity 1.13 meq/g of dry membrane; area resistance $3.36 \text{ }\Omega\text{cm}^2$; permselectivity 94% in 0.013 N against 0.0067 N NaCl . 2) A reverse electrodialysis membrane, polyethylene based; ion-exchange capacity 0.8 meq/g of dry membrane; area resistance $8 \text{ }\Omega\text{cm}^2$; permselectivity 96% in 0.0133 N against 0.0067 N NaCl . Most of the reported results are related to the Selemion membrane. The other membrane produced similar results, which confirmed all the conclusions drawn from the experiments on the Selemion membrane.

The flicker noise was observed on a dual-beam oscilloscope, Tectronic 5351, as current fluctuations. A resistance r was inserted in series with the cell resistance $R(t)$, and the voltage across r was put into the oscilloscope. As r was chosen to be much smaller than $R(t)$, the oscilloscope followed the current fluctuations across the cell at an essentially constant voltage. The detection band width of the experimental set-up was $0.03\text{--}5000 \text{ cps}$. For the experiments at 0.01 N KCl , we kept r at $4.7 \text{ k}\Omega$.

The Laser Beam Scattering Experiment

A coherent narrow beam of light of $\sim 0.01 \text{ cm}$ in diameter, from a HeNe 1 mW laser, was focussed in front of the membrane. It entered one of the cell compart-

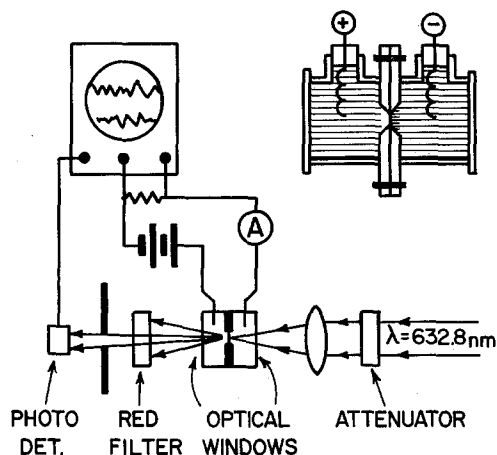


Fig. 1. A schematic representation of the conduction cell, the electric circuit and the optical system of the laser beam experiment

² Produced by Asahi Glass, 1-2 Marunouchi, 2-Chome, Chiyoda-Ku, Tokyo, Japan

ments through an optical window, as shown in Figure 1. Upon passing through the membrane, the beam broadened, having been scattered by the membrane, which was translucent, like frosted glass. The electrolyte solution was "labelled" with $\sim 10^9$ scattering centers per cc, using mono-dispersed latex particles of $0.2\text{ }\mu\text{m}$ in diameter. The light intensity was detected by a photodiode after passing through a narrow slit and a red filter, and its fluctuations were displayed on the dual-beam oscilloscope, in parallel with the membrane noise. As explained in subsection Results below, the "light noise" was caused by the number-fluctuations of the scattering particles in the narrow light beam, as well as by the fluctuations in the interference pattern of the coherent light, due to the motion of the scattering particles. Convection currents across the laser beam produced such fluctuations, and were therefore directly observed by the photocell. The "light noise" was not detectable, within the sensitivity limits of our system, when the electrolyte solution was filtered, to be clean of dust, and no latex particles were added.

Results

In this section we present the results of a series of experiments designed to examine the above mentioned considerations and predictions.

a) The Chronometric Measurement of Current Drop and Onset of Noise

Upon closing the circuit, the current always started with a maximum value, from which it dropped steeply, then leveled off at a steady-state far below its initial value. In Figure 2, Channel 1 represents a typical behavior of the current as a function of time at sufficiently high current densities. In this case, the initial density was 34.5 mA/cm^2 . As the depletion layer developed, the current dropped to its half-value in

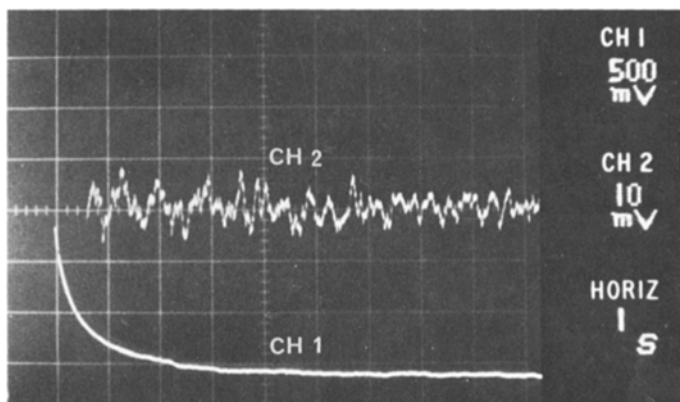


Fig. 2. Current drop (lower trace, Channel 1) and onset of noise (upper trace, Channel 2), corresponding respectively to current densities of 9.4 mA/cm^2 and 0.19 mA/cm^2 per division, at 0.01 N KCl and room temperature. One horizontal division corresponds to 1 s

about 400 ms, and approached a steady state of about 5.8 mA/cm² in about 30 s. The resistance of the circuit increased, respectively, from the initial value of 28 k Ω (cell \sim 23 k Ω , membrane \sim 0.3 k Ω and oscilloscope \sim 4.7 k Ω) to 56 k Ω in about 400 ms, then to 166 k Ω . The rise in resistance was caused solely by the formation of the depletion layer. It was accompanied, necessarily, by an excess heating of the depleted layer which reached a maximum after 400 ms, at which point its resistance equalled that of the rest of the circuit, and settled to about 0.013 cal/s/cm² in the steady state. Such heat dissipation may be sufficient to set up a density gradient which, together with the concentration gradient create turbulent convection.

Channel 2 of Figure 2 represents the flicker noise as the ac component of the current, amplified by 50 compared to the full current in Channel 1. It is seen that the flicker noise starts at the latest immediately after the current dropped to its half-value³, which is the point of the maximum heat production in the depletion layer. This may support the suggestion that heating is part of the mechanism of the flicker noise.

It is important to note here, that current density profiles such as in Figure 2 are difficult to reproduce, unless the system is allowed sufficient time, of the order of several minutes at the least, to relax towards equilibrium in both temperature and concentration.

It should also be noted that a small reduction of the e.m.f. of the system, due to the opposite concentration changes across the membrane, of the order of a small fraction of a volt, might also be considered. It was, however, negligible as compared with the voltage across the cell, which was of the order of 10 volts.

b) Weak and Strong Current Densities

There exists a critical current density, below which flicker noise is not observed [13]. This critical current density defines a sharp boundary between regimes of weak and strong current densities, and is an increasing function of the electrolyte concentration. As the current density increases above its critical value, the ratio $\overline{\delta J^2}/\bar{J}^2$ between the noise power and total current power increases gradually, until it reaches a limiting value. Figure 3 represents this ratio as a function of the current density J , for 0.1 N KCl; $\overline{\delta J^2}$ was estimated by squaring the width of the noise patterns, as observed on the photographic records of the oscilloscopic displays. The proportionality between the power spectrum of flicker noise and the square of the current, which was considered as a characteristic property of flicker noise [22] is compatible with our findings only for the above mentioned limit of strong current densities, where $\overline{\delta J^2}/\bar{J}^2$ is constant. This proportionality seems intuitively in agreement with the suggestion that power dissipation, which is proportional to \bar{J}^2 , is the source of noise [7]. The deviation from this proportionality toward a critical current density, seems also to be in agreement with our suggestion that turbulent convection currents are the source of noise. A sudden transition from laminar to turbulent flow is an

³ Note that the ac trace of Channel 2 displays an apparent delay time. This delay is due to a fast ac voltage transient which is beyond the range of the oscilloscope screen. Its entrance to the screen was too faint to be recorded at the photographic exposure level

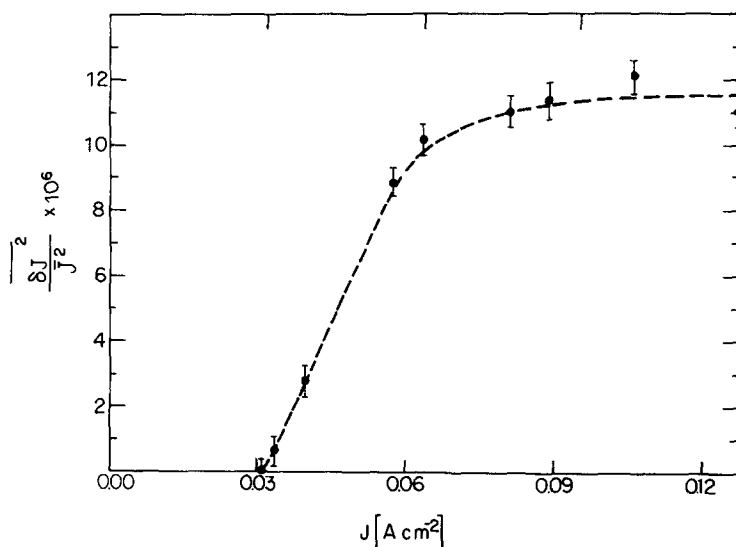


Fig. 3. Ratio of noise power to current power as a function of current density, for 0.1 N KCl at room temperature

inherent property of fluids, and so is also the gradual build-up of turbulence above the critical point.

The steady-state resistance of the system was maximal below the critical current density, and decreased gradually beyond it. This decrease of resistance with increase of current density, seems to be caused by the turbulent mixing of the depleted layer, which becomes stronger as the current density increases. The initial current at $t = 0$, i.e. preceding the formation of the depleted layer, obeyed Ohm's law, as expected.

c) Temperature Dependence

The flicker noise decreases with decreasing temperature, as is seen in Figure 4, and as should be expected. The reason is two-fold: a) As the thermal expansion coefficient tends to zero approaching 4°C , the buoyant forces reduce accordingly. b) As the viscosity increases with decreasing temperature the strength of the convection currents decreases accordingly. Also, the onset of instability should shift towards higher gradients, and therefore higher electric current densities.

It would be wrong, however, to expect the noise to disappear when the equilibrium temperature of the system is 4°C . The temperature gradients created by the current imply always a finite range of temperature change in the depleted layer, and therefore the establishment of some density gradients at all temperatures. Furthermore, the concentration gradient is present at all temperatures.

Note here again that it is absolutely necessary to allow the system to reach equilibrium with respect to temperature and concentration in order to observe the true temperature-dependence of the noise. If the current is allowed to flow for some

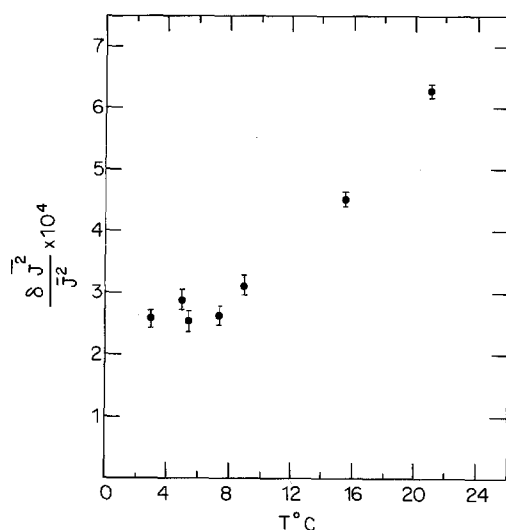


Fig. 4. Ratio of noise power to current power as a function of temperature, at strong current densities ($\sim 10 \text{ mA/cm}^2$), and 0.01 N KCl

time, the temperature dependence is masked, as the temperature in the vicinity of the membrane rises gradually.

d) The Effect of Increased Bulk Viscosity in the Depleted Layer

If turbulent convection is the source of noise, then whenever convection or its turbulent nature are reduced, noise must also be reduced. To check this assertion we added poly(vinyl-pyrrolidone), a water-soluble non-ionic polymer, to *one* of the electrolyte compartments, thus increasing the bulk-viscosity of the solution in this compartment by 70%, while leaving the ionic conductance unchanged to within 1–2%. When the direction of the current was such as to carry the K^+ ions from the compartment of low viscosity to that of high viscosity, the pattern of the flicker noise remained the same as in the corresponding experiments without added polymer. However, when the current flowed in the reverse direction, namely from the more viscous compartment to the less viscous one, the noise was reduced very considerably. Figure 5 represents the flicker noise in the two cases. It seems that the higher viscosity in the depleted compartment shifted the convection current from the turbulent towards the laminar regime thus reducing the noise considerably while allowing at the same time the heat produced in the depleted layer to dissipate.

e) Orientation in the Gravitational Field

Another proof that convection is the cause of the flicker noise was obtained by tilting the conduction cell so that the selective membrane was positioned horizontally. Block and Kitchener [1] observed that the polarization of horizontal ion-exchange membranes changed with the direction of current. Our findings on noise are in full agreement with theirs on polarization. If the ionic current through the

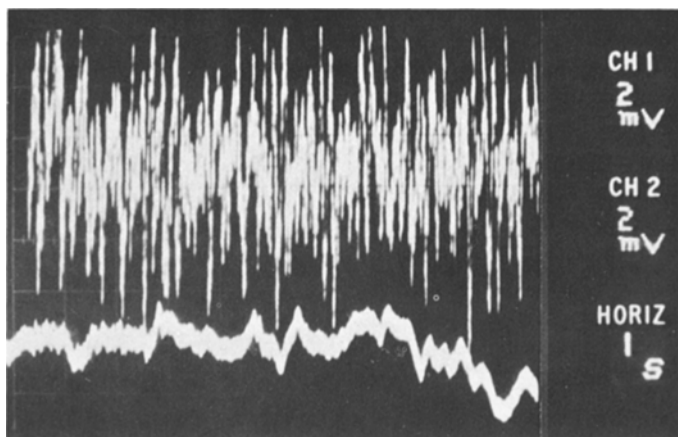


Fig. 5. Reduction of noise by increased bulk viscosity in the compartment of the depleted layer at 0.01 N KCl, 13 mA/cm² and room temperature. Channel 1, upper trace — current flows from less to more viscous solution; Channel 2, lower trace — the reverse direction

membrane moved downward, the noise resembled that of vertical membranes, while if the current was directed upwards, the noise as well as the current itself was reduced considerably. Theoretically one should expect the complete disappearance of noise when the current moved upward. In this case both the depleted layer on top of the bottom compartment and the enriched layer at the bottom of the top compartment were expected to be stable hydrodynamically. The occurrence of some noise had to be attributed to boundary effects, or to the inhomogeneity of the membrane. The latter caused the electric current near the surface of the membrane to vary from point to point, due to differential heating and concentration effects which set-off convection currents in the depleted layer. Note however that when the heat generated is not dissipated fast enough, convection may be generated by degassing and boiling in the depleted layer [1].

f) Direct Observation of Correlation Between Flicker Noise and Convection Using a Laser Beam

In order to observe directly the convection current created by the electric current, we performed the laser beam experiment described in the Section Materials and Methods. Given the concentration of latex particles (10^9 per cc), the diameter of the laser beam, and the thickness of the turbulent layer (of the order of 10–100 μ m), an average number N of about 100–1000 latex particles was expected to be found within the illuminated volume of the depleted layer. When the convection current moved across the laser beam, this number of N particles fluctuated by the order of \sqrt{N} . The laser beam was scattered coherently by the particles, and the forward light, passing through a slit to the photocell, showed an interference pattern. This pattern fluctuated both due to the motion of the illuminated particles and the fluctuation in their number. The photocell current fluctuated accordingly, thus offering a direct

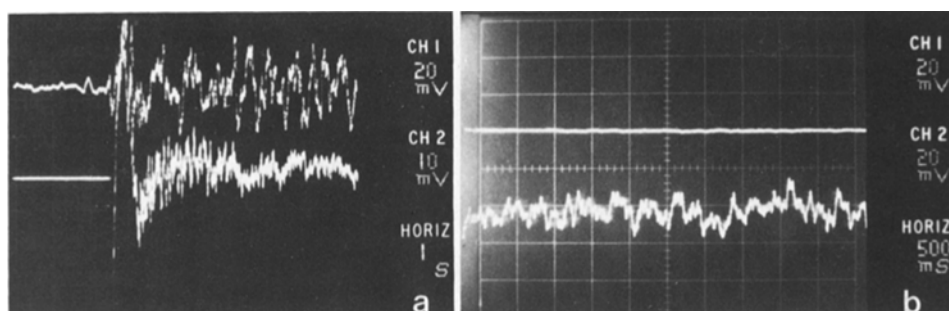


Fig. 6. Current noise (Channel 2, lower trace) vs. “light noise”, (Channel 1, upper trace) showing their simultaneous onset. **a** The laser beam is focussed on the depleted layer; **b** The laser beam is focussed on the enriched layer; at 0.01 N KCl, 12 mA/cm² and room temperature

probe of the convection. This “light noise” was recorded on the dual beam oscilloscope simultaneously with the electric current noise. When no current passed through the membrane little “light noise” was observed, since Brownian motion alone was too slow to cause large fluctuations. As soon as current noise developed in the depleted region, the “light noise” appeared simultaneously as is seen in Figure 6a. It should be noted that the “light noise” was observable also in the low current regime of laminar convection, but its magnitude was very much smaller.

When the direction of the current was reversed, the narrow laser beam passed through the enriched side of the membrane. Here the “light noise” was not observed, as is seen in Figure 6b. In this case the depleted region occurred beyond the membrane; and although convection currents did form there, they did not contribute anything to the “light noise”. The reason is that the laser beam was well-focussed only in front of the membrane. Due to the translucent nature of the membrane, as noted in the Section Materials and Methods, the laser beam emerged from the membrane scattered and unfocussed. Therefore the illuminated part of the depletion layer was now much larger, not sharply defined and less intensely illuminated. As a result no flickering of light from the turbulent depletion layer was observed.

The absence of “light noise” when the laser beam is focussed on the enriched layer is of particular interest, because it proves that there are no significant convection currents in the enriched layer. It establishes conclusively the asymmetry of the convection flow patterns on both sides of the membrane. This observation is relevant to the problem of the relative importance of thermal and concentration gradients as sources of turbulence in the depleted layer. We shall return to it in the Discussion Section.

Discussion

In this section we shall present some of the conclusions as well as the unresolved problems which follow the experiments in the previous section.

The laser experiment [Results, Subsection (f), Fig. 6] showed how convection in the depleted layer appeared and disappeared coincidentally with the flicker noise. It

did not indicate explicitly whether the convection was turbulent or laminar. It did, however, show that the convection in the enriched layer was unnoticeable relative to that in the depleted layer. Considering all other experiments, it seems very likely that the convection in the depleted layer was vigorous and turbulent, while the convection in the enriched layer was slow and presumably laminar. This substantial asymmetry of behavior of the two layers was also indicated by the bulk viscosity experiment [Results, Subsection (d), Fig. 5]. Such an asymmetry is expected to develop only after the current exceeds a "limiting current density" [6, 25] (LCD), at which the ionic concentration at the surface of the membrane reached a minimum which is a small fraction of the bulk concentration. Above the LCD the depleted layer is composed of two parts: The full depletion layer near the membrane, which has a very low ionic concentration and a correspondingly high resistivity, and the diffusion layer in which, according to Nernst, the concentration increases linearly up to the bulk concentration. As the current is increased above the LCD, the diffusion layer must grow steeper (since the current in this layer is proportional to the concentration gradient), and the full depletion layer probably tends to become wider. The changing concentration profile, together with the growing temperature gradient, makes the convection in the depleted layer grow with increasing current and ultimately leads to hydrodynamic instability, namely to the onset of turbulence and current noise. The current at which noise first appears [Results, Subsection (b), Fig. 3] is the critical current density (CCD). According to these considerations, the CCD has to be larger than the LCD. Cooke [6] obtained for the LCD in KCl solutions values of ~ 6 mA/cm² and ~ 10 mA/cm² at 0.05 N and 0.1 N respectively. Our measured CCD at 0.1 N KCl is ~ 30 mA/cm², namely three times larger than the LCD. In the range of current densities between LCD and CCD the resistance in the depleted layer is the highest; the onset of turbulence reduces the resistance, due to mixing.

It would be interesting to determine the relative contribution of the concentration and the temperature profiles in the depleted layer to the buoyant forces. This would require, even in the case of low current regime and laminar convection, the solution of the heat conduction, Nernst and Stokes-Navier equations. The solution should depend on the particular shape, size and orientation of the membrane. This is a rather difficult task in general [3, 16, 21]. Its particular case, that of the limit of hydrodynamic stability in the horizontal orientation experiment [Results, Subsection (e)] bears similarity to Bénard systems [3].

However, even a rough estimate of the orders of magnitude of the concentration and temperature changes in the depleted layer, may be of some interest. From the chronometric measurements of the current drop [Results, Subsection (a), Fig. 2] one obtains the heat production rate in the depleted layer at steady state current as 0.013 cal/(s) (cm²). To dissipate this heat solely by conduction would require a temperature gradient of ~ 10 °C/cm, since the conductivity of water is ~ 0.0014 cal/(s) (cm²) (°C/cm). This amounts to a density gradient of $\sim 3 \cdot 10^{-3}$ since the thermal expansion coefficient of water is $\sim 3 \cdot 10^{-4}$ cm³/°C at room temperature. The density gradient due to the depletion of salt seems to be between one and two orders of magnitude larger than that due to heating in this experiment. It may be estimated from the density difference between 10^{-2} N KCl and pure water, which is $\sim 5 \cdot 10^{-4}$ g/cm³, divided by the thickness of the depleted layer. The latter may be estimated as $\sim 3 \cdot 10^{-3}$ cm from Nernst's formula relating the current density to the

concentration gradient. It should be noted, however, that these estimates are subject to significant changes in consideration of the complex structure of the depletion layer which, as we have seen, is composed of the full depletion layer besides the diffusion layer. Furthermore, the effect of convection, whether laminar or turbulent, should be properly taken into consideration and may change the estimates significantly. Thus it is impossible at present to evaluate the relative effect of the concentration and thermal profiles on the flicker noise in our experiments. It is worthwhile to note in this connection that the temperature experiment [Results, Subsection (c), Fig. 4] did not help to distinguish between thermal and concentration gradients as causes for the onset of turbulence. Reduction of the thermal expansion coefficient and the increase of viscosity coefficient might both contribute to the reduction of noise with temperature, and their relative effect could not be separated.

All the above experiments taken together support, we believe, the theory presented here about hydrodynamic turbulence as a source of flicker noise. They leave, however, as we have seen, many questions for further study. Perhaps the most interesting question is whether hydrodynamic turbulence may be a source of noise in other types of membranes. In biological membranes the current flows through narrow ion-selective pores; in some synthetic high resistance membranes, the pores may be nonselective. In all such membranes the pore dimensions are very much smaller than the geometric parameters of the membranes studied here. The theoretical difficulties in analyzing such systems in detail are enormous. However, an experimental approach such as the one followed in this paper might help to determine whether the noise in those membranes is generated in the solution near the surface of the membrane, and whether it is correlated with convection.

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