FLUCTUATIONS IN A SMALL VOLUME OF ELECTROLYTE

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ABSTRACT

Fluctuations in a Small Volume of Electrolyte

Measurement of a current dependent noise spectrum for a small volume of electrolyte is reported. The noise is greater in magnitude and has a frequency dependence different from that predicted by thermodynamic theory. The spectrum is compared with similiar results obtained by other experimenters and is reported here as an observed phenomena.

ACKNOWLEDGEMENTS

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FLUCTUATIONS IN A SMALL VOLUME OF ELECTROLYTE

In attempting to develop a model for the mechanism of desalination by reverse osmosis, one would like to have measured parameters which can reveal something about the behavior of ions inside membranes. One such parameter is that of noise or fluctuations. Noise measurements are desirable not only because noise can mask other experimental results, but also because some of the noise sources themselves can be traced to the behavior of the ions. In particular, this paper deals with an attempt to measure the noise due to energy (or thermal) fluctuations in a small volume of salt water.

Theory and Previous Work

From thermodynamics, temperature fluctuations in a small volume of a solution are given by

$$\overline{T_N^2} = \frac{kT^2}{C_p} \tag{1}$$

where T is the constant temperature of the large volume, k is Boltzmann's constant, and C_p is the heat capacity at constant pressure.[1] These thermal fluctuations can be observed as voltage fluctuations since the electrical resistivity of an electrolyte is temperature dependent. A current flowing through the electrolyte in a capillary (the small volume) yields a voltage drop, V=IR, which fluctuates with the changes in resistance produced by the thermal fluctuations. From Eq. (1), the integrated mean square noise voltage is then given by

$$\overline{V_N^2} = \frac{V_c^2 k}{C_p}\left[\frac{T}{R}\frac{\partial R}{\partial T}\right]^2 \tag{2}$$

where V_c is the dc voltage across the capillary, and R is the

*The format for this paper was taken from The Journal of Chemical Physics.

resistance of the capillary.[2] Noise consistent with Eq. (2) has been observed by Weissman and Feher with an electrolyte of the following composition (by weight): 15% glycerol, 85% $ZnCl_2$, and 0.03% HCl.[2] The complexity of this solution reflects a desire to have a high temperature coefficient of resistivity which yields a more easily observed level of noise. The same work also revealed a frequency dependence for the noise of $f^{-1.7}$ for frequencies above 100 Hz. This dependence is also in agreement with thermodynamic theory.[2]

A different noise spectrum (the importance of which will become apparent) has been observed by Hooge and Gaal for small volumes of electrolyte.[3] Their results show a noise voltage given by

$$\overline{V_N^2} = \frac{b}{N} V_c^2 \frac{\Delta f}{f} \qquad (3)$$

where V_c is the dc voltage across the capillary, Nis the number of free charge carriers, Δf is the bandwidth, f is the frequency, and b is a constant determined experimentally. Eq. (3) however, unlike Eq. (2), is not given by thermodynamic theory; it is simply a relation based on experimental results. Therefore, its importance lies in the fact that it is an observed phenomena and not in its support of theory.

Design of the Cell

The ultimate goal of desalination being kept in mind, a 5% (by weight) solution of NaCl in water was chosen as the electrolyte. (Neither of the two previously described works involved NaCl solutions.) The specific heat c_p for this solution was

$$c_p = 4.065 \text{ J/K-ml} \quad .[4]$$

As derived from data taken from the International Critical Tables,

$$\frac{T}{R}\frac{\partial R}{\partial T} = 5.27 \quad .[5]$$

The two factors in Eq.(2) which can be manipulated to achieve an observable noise voltage are then V_c and the volume of the capillary contained in the factor C_p.

In calculating the desired dimensions for the cylindrical capillary, one must ensure that the Johnson noise (which is frequency independent) will not be so great as to mask the desired thermal fluctuations. The Johnson noise per unit bandwidth is given by

$$\overline{V_J^2} = 4 R_c k T \tag{4}$$

R_c, the resistance of the capillary, is given by

$$R_c = \frac{\rho l}{A} \tag{5}$$

where p is the resistivity of the solution, l is the length of the capillary, and A is its cross-sectional area. Since

$$\overline{V_N^2} \propto \frac{1}{Al}$$

and

$$\overline{V_J^2} \propto \frac{l}{A}$$

one obtains

$$\frac{\overline{V_N^2}}{\overline{V_J^2}} \propto \frac{1}{l^2}$$

so that l should be made as small as possible. However, in order to have a well-defined, uniform electric field inside the capillary, it is desirable to have $l > r$.[6] Taking these factors into account, the values chosen for l and r were

$$r = 0.04 \text{ mm} \quad \text{and} \quad l = 0.97 \text{ mm}$$

Finally, V_c could be adjusted to yield an observable noise (with its upper bound being set by the maximum power dissipation of the capillary).

Fig. 1 shows the capillary mounted in the cell. The capillary was formed by pouring a plastic resin around a slightly lubricated copper wire and than hardening the resin with a catalyst. The wire was withdrawn after hardening, leaving a cylindrical hole, the capillary, in a plastic disk. The disk was then sanded to its final thickness, the length of the capillary. Finished dimensions of the capillary were

$$r = 0.06 \pm 0.01 \text{ mm} \quad \text{and} \quad l = 1.15 \pm 0.02 \text{ mm}$$

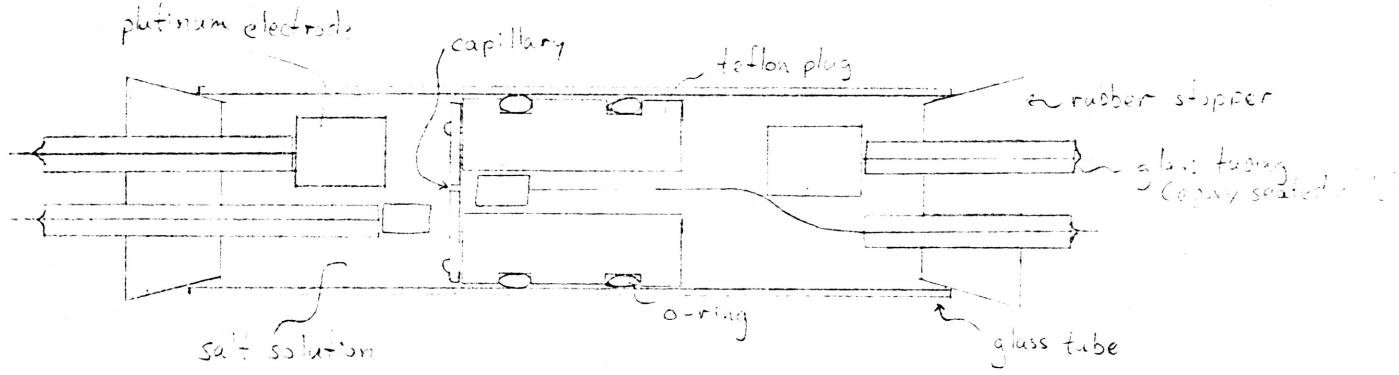

Fig. 1 Cell Design

r was measured with the aid of a microscope and l was measured with a micrometer. These values, when inserted into Eq. (5), and taking into account the spreading resistance[7], yield a value of R_c which agrees with the value of

$$R_c = 16 \times 10^3 \text{ ohms}$$

obtained experimentally.

The inner electrodes of Fig. 1 were used to measure the noise voltage, and the outer electrodes were used to provide the constant current necessary to produce voltage fluctuations from resistance fluctuations. All current flowed through the capillary since the teflon and glass are insulators.

Electronics

The electrical arrangement for the experiment is illustrated in Fig. 2. Several items warrant explanation. The signal generator is used to introduce a known test signal across the 100 ohm resistor. The gain of the entire system can then be determined by noting the output at the chart recorder. Resistor R_s is large compared with R_c to provide an almost constant current for small fluctuations in R_c. The two opposing power supplies are so arranged to allow one to obtain $V_s=0$ without turning a power supply off or down so low that it would stop regulating its output sufficiently. The aluminum shield (a piece of aluminum pipe) was essential in eliminating noise from extraneous sources.

The signal arriving at the amplifier is composed of V_c, the dc component, and the fluctuation or noise voltage. The noise is amplified and fed into a wave analyzer (bandwidth=7 Hz) which measures the root mean square noise voltage for the frequency band centered at a selected frequency. The analyzer drives the chart recorder, and one can therfore obtain the noise voltage as a function of frequency by sweeping over the desired range.

Experimental Method

Chart recordings of the amplified noise were taken for $V_s=0$, +30,+40,+50,+60 and -60V over a frequency range from 100 to 1000 Hz.

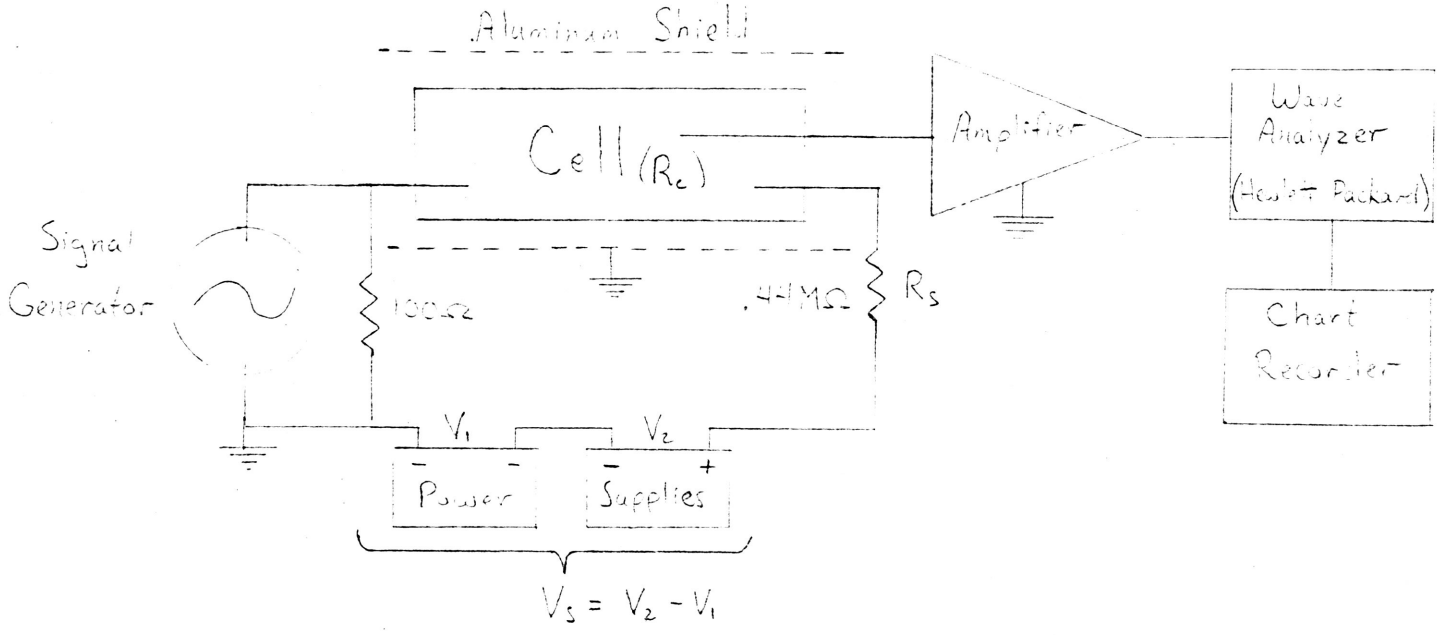

Fig. 2 Electronics

V_C in Eqns. (2) and (3) can be found from V_S by

$$V_c = \frac{R_c}{R_s + R_c} V_s = 0.035\, V_s$$

The V_C=0 noise measurement was taken to determine the background noise, primarily consisting of Johnson noise. Mean square noise voltages for V_C non-zero were then given by

$$\frac{\overline{V_N^2}}{Hz} = \frac{\overline{V_{N+B}^2} - \overline{V_B^2}}{7\ Hz} \qquad (6)$$

where the 7 Hz factor corresponds to the bandwidth of the analyzer, and V_B is the background noise. The measurement for V_S= -60V was taken to reveal any polarization of the cell. The signal generator was then used to input a test signal of known amplitude (much greater than the noise voltage) and frequency. Gain for the system was found to be constant over the frequency range of interest. With the gain determined, RMS noise voltages could be read off the chart recordings.

Experimental Results

From the V_S=0 noise measurements, the background noise was found to be

$$\frac{\overline{V_B^2}}{Hz} = 2.93 \pm 0.40 \times 10^{-16} \frac{V^2}{Hz}$$

From Eq. (4), the expected Johnson noise is

$$\frac{\overline{V_J^2}}{Hz} = 4R_cKT = 2.63 \times 10^{-16} \frac{V^2}{Hz}$$

Therefore, the background noise for the cell was almost entirely Johnson noise.

Fig. 3 illustrates the noise spectrum for the frequency range of 100 to 700 Hz. Above 700 Hz, the noise voltage was too close to the background noise for any meaningful difference in Eq. (6) to be obtained. The theoretical value for the integrated noise is calculated from Eq. (2) to be

$$\overline{V_N^2} = 2.99 \times 10^{-17}\ V^2$$

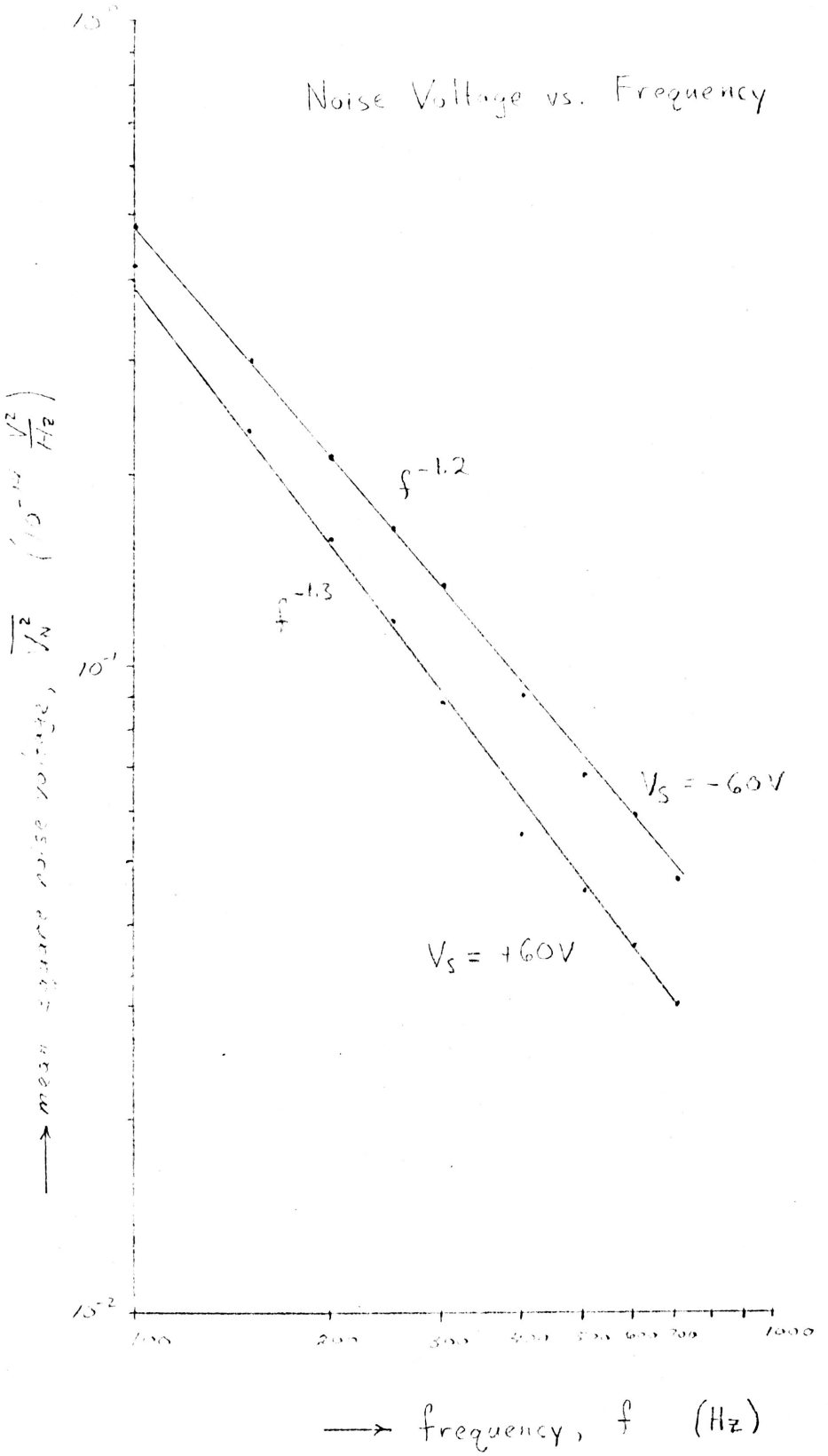
Noise Voltage vs. Frequency
$f^{-1.2}$
$f^{-1.3}$
$V_S = -60V$
$V_S = +60V$
10^{-1}
10^{-2}
frequency, f (Hz)

Fig. 3

When compared with the spectrum shown in Fig. 3, one realizes that the noise observed was almost certainly not due to thermal fluctuations. The integrated noise from Fig. 3 would be much greater than that predicted by theory. However, the observed noise is certainly dependent on the current flowing through the cell. This dependence is shown in Fig. 4 where the noise demonstrates a dependence on the order of V_s squared. What then is the source of this noise?

Noise due to insufficient regulation in the power supplies was suspected but ruled out for the following reasons:

1) The power supplies are still turned on for $V_s=0$ and should therefore produce noise even though they add to zero. Yet the background noise matches the predicted value for the Johnson noise.

2) A 15,000 ohm resistor was put in place of the cell in Fig. 2; changes in V_s produced no noticeable changes in the noise voltage as would be expected if power supply regulation was a problem.

At present, the best explanation for the observed noise spectrum is a comparison with the results of Hooge and Gaal even though differences between the experiments make this comparison somewhat questionable. Their results show a dependence given by Eq. (3).

$$\frac{\overline{V_N^2}}{Hz} = \frac{b}{N} V_c^2 \frac{1}{f} \qquad (3)$$

This equation contains the observed V_c squared dependence, as well as a f^{-1} dependence which the observed noise spectrum comes close to matching. After calculating the number of free charge carriers N from the concentration of the solution and the volume of the capillary, one obtains a value for b, the experimental constant, of

$$b \cong 1200$$

The typical value for b found by Hooge and Gaal was

$$b \cong 10^3$$

Conclusions

In summary, a current dependent noise spectrum has been observed for a small capillary containing a salt solution. This noise is much

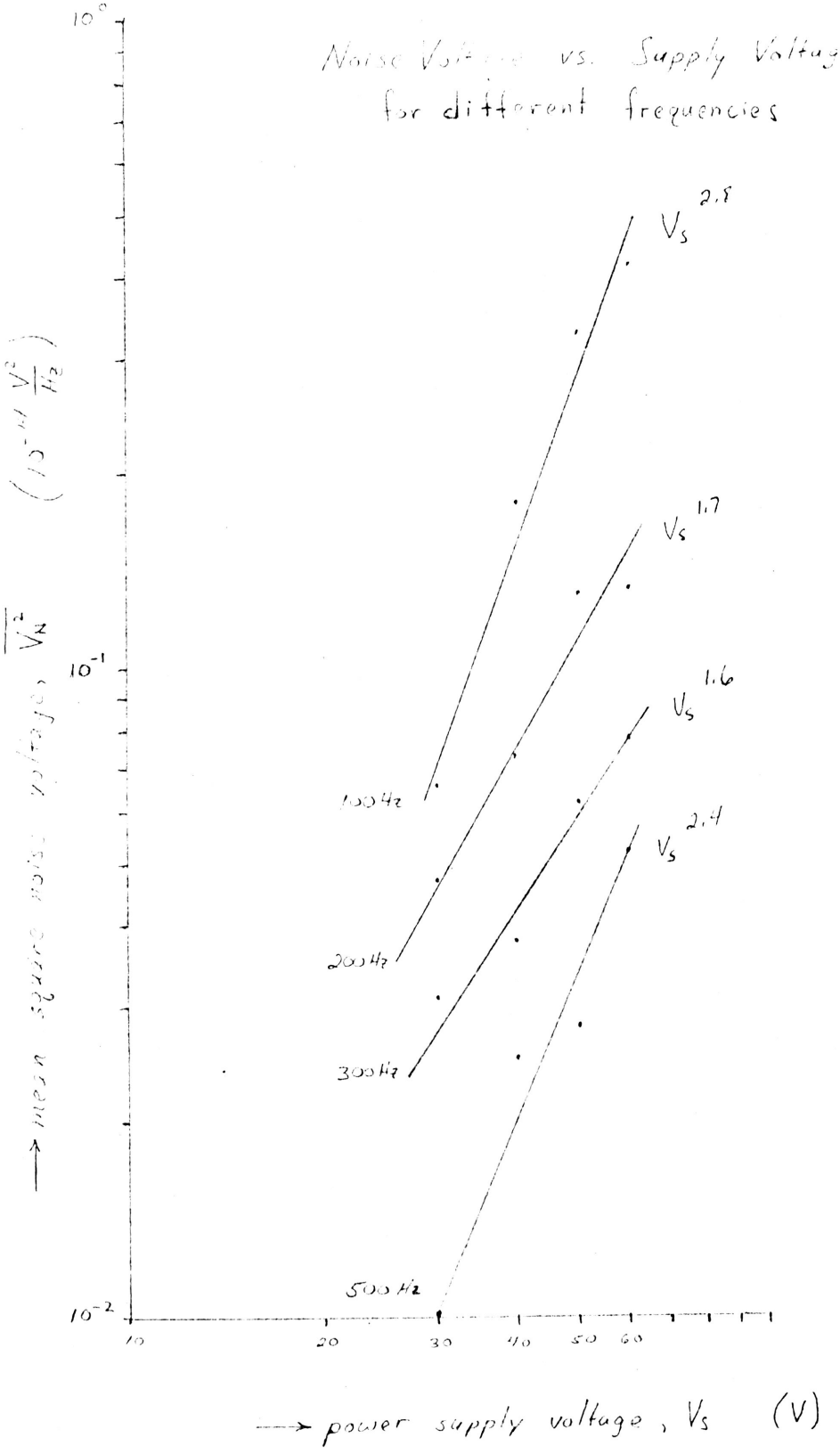
Noise Voltage vs. Supply Voltage
for different frequencies
10^0
10^{-1}
10^{-2}
mean square noise voltage, $\overline{V_N^2}$ (10^{-14} $\frac{V^2}{Hz}$)
100 Hz
200 Hz
300 Hz
500 Hz
V_s 2.8
V_s 1.7
V_s 1.6
V_s 2.4
10
20
30
40
50
60
power supply voltage, V_s (V)

Fig. 4

greater than that predicted by thermodynamic theory and will therefore certainly prevent any observation of the thermal fluctuations unless it is reduced. The observed noise spectrum can, at least qualitatively, be compared with that found (but not explained by theory) by other experimenters. Differences in solutions, capillary dimensions, etc. could account for the difference in the experimental constants; however, such speculation must be tested through further experimentation.

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