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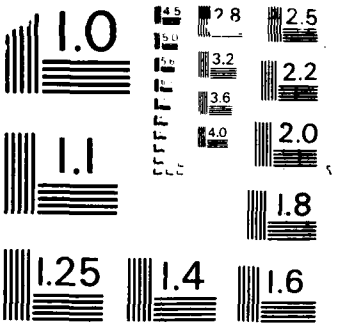

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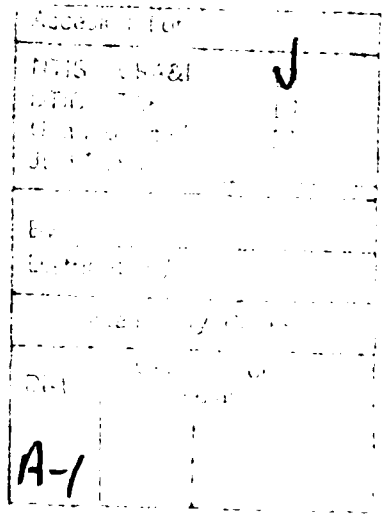

THE KINETICS OF CONTACT NOISE IN Naβ"ALUMINA

by

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Abstract

The kinetics of interfacial chemical reaction noise at sodium amalgam and NaI propylene carbonate contacts to Naβ"alumina are examined by determining the time and temperature dependence of the noise. The rate constant for the reaction noise is larger for amalgam contacts and increases with sodium concentration in both cases. The noise is thermally activated with an activation energy of 0.5eV, which is similar to that of bulk diffusion noise in Naβ"alumina.

INTRODUCTION

Contact noise ascribed to chemical reactions at the interface between liquid electrodes to Naβ"alumina has been observed for several electrode materials, both ohmic and blocking (1,2). In general, the contact noise levels decrease with time such that Nyquist noise of the bulk solid electrolyte and diffusion noise of the mobile ions can be detected. In the case of pure mercury contacts, a chemical reaction rate constant of 4500 sec^{-1} is observed at room temperature and the noise is associated with amalgamation reactions at the interface (3).

All electrode materials examined to date also exhibit chemical reaction noise having a much smaller rate constant (4). The kinetics of this reaction are reported here for sodium amalgam and NaI in propylene carbonate electrodes to Naβ"alumina, both of which are known to produce stable, low noise contacts after ageing.

EXPERIMENTAL PROCEDURE

Commercial sodium β"alumina ceramic samples (5), 1x1x0.2 cm^3 and 1x0.5x0.2 cm^3, are carefully polished with #500 carborundum paper, baked in air and then provided with sodium amalgam or propylene carbonate solution electrodes by epoxying the ceramic into the sides of plastic tubes. Amalgams of different concentrations are prepared by electrolyzing a concentrated NaCl solution. Similarly, weighed amounts of NaI are dissolved in a known volume of propylene carbonate to achieved differing sodium concentrations in the electrode material. Voltage fluctuations of the newly prepared contacts are measured at the input of a PAR 113 preamplifier and analyzed digitally using an A/D conversation and FFT system. The time and temperature dependence of the noise is determined at several frequencies in order to evaluate the behavior of the noise decay.

RESULTS AND DISCUSSION

Typical noise spectra of sodium amalgam and NaI propylene carbonate contacts to Naβ"alumina ceramics are shown in Figure 1 for different times after preparation. The slope of -2 suggests a Lorentzian noise spectrum associated with a non-equilibrium reaction having a single relaxation time

(1,2). After ageing, the noise of both contact materials decreases sufficiently for Nyquist noise of the bulk electrolyte to be observed at frequencies above about 10 Hz. Before attaining the equilibrium state, the amalgam electrode always shows much higher noise levels than the propylene carbonate. Low noise contacts of both electrode systems can be established in a few hours for all the concentrations investigated here except for most the dilute amalgam (0.19 mole% Na), for which the low frequency excess noise is still observable after ageing twenty-four hours.

The interfacial reaction noise for both electrodes decays exponentially with time, Figure 2. The voltage fluctuations at a given frequency as a function of the ageing time t after contact preparation can be written as

$$S(f,t) = A\exp(-kt) \qquad (1)$$

where A and k are constants dependent upon concentration. Table 1 lists experimentally determined values for different concentrations of sodium in the liquid electrodes. Clearly, the rate constant in the case of the amalgam electrodes is much greater than that for the NaI propylene carbonate contacts, and both increase with sodium concentration. Also, the largest rate constant, $3.16\times10^{-3}\text{sec}^{-1}$, places the characteristic frequency of the Lorentzian spectrum at $k/2\pi = 5\times10^{-5}$ Hz, well below the range of the experimental measurements illustrated in Figure 1. In the concentration interval investigated here, both electrodes show a linear relationship between the rate constant and the concentration of sodium species in the liquid electrodes, Figure 3, indicating a first order reaction.

As illustrated in Figure 4, the rate constant is thermally activated. The data yield an activation energy of 0.5 eV/mole, which is close to the activation energy of bulk current noise attributed to diffusion of the mobile sodium ions (6). The similar activation energies suggest that there exists the same dominating mechanism in both processes. Since the sodium ions are the sole ionic species mobile within the Naβ"alumina, they must be involved in the reaction responsible for forming equilibrium contacts. Possible reactions, then, are illustrated in Equations (2a) and (2b) in which an interaction is assumed to exist between the sodium ions in the Naβ"alumina and the sodium species in the electrodes:

$$(Na^+)\ \beta''Al_2O_3 <-> (Na+)_{NaI(PC)} \qquad (2a)$$

$$(Na+)\ \beta''Al_2O_3 <-> (Na)_{Amalgam} \qquad (2b)$$

The first order reaction derived from the concentration dependence of noise decay rate shows that the dominating reaction is a unimolecular process. The reaction rates for the two types of contacts are different at the same sodium concentration, which is likely to result from the dissimilar chemical state of the Na species in the amalgam compared to the propylene carbonate solution.

Figure 4 also illustrates the temperature dependence of the pre-exponential factor A in Equation (1), which corresponds to the non-equilibrium reaction noise at t=0. The activation energy is 0.58 eV.

However, further calculation by inserting the extrapolated noise and rate constant into Equation (7) of Ref. 2,

$$S(V,f) = \frac{4Nk^3e^2Z_c^2}{k^2+\omega^2} \tag{3}$$

yields unreasonably high contact impedances. On the other hand, we can insert the temperature-dependent terms into Equation (3) to calculate the activation energy of the impedance involved in the charge transport for the non-equilibrium reaction,

$$S(V,f,T) = \frac{4N(T)k^3(T)e^2Z^2(T)}{k^2(T)+\omega^2} \tag{4}$$

At frequencies much higher than the turnover frequency,

$$S(V,f,T) \approx \frac{4N(T)k^3(T)e^2Z^2(T)}{\omega^2}$$

$$= \frac{4N_ok_o^3e^2Z_o^2(T)}{\omega^2} \exp(-E_N-3E_k+E_Z) \tag{5}$$

where E_N, E_k and E_Z stand for the activation energy for reaction species, rate constant and impedance, respectively. N_o, k_o and Z_o are the pre-exponential factors. After inserting the activation energies 0.58 eV, E_N=0.75 eV and E_k=0.5 eV into Equation (5), we obtain E_Z=0.84 eV. This value is reasonable if both the ion transport processes in bulk solid electrolyte and at the electrolyte-electrode interface are concerned.

CONCLUSIONS

1. The chemical reaction noise generated at the interface between sodium amalgam or NaI propylene carbonate solution contacts to Naβ"alumina decays exponentially with time and equilibrium low noise contacts can be attained by ageing the contacts for several hours.

2. The rate constant for the interfacial reactions increases linearly with sodium concentration in the electrodes, which indicates a first-order reaction.

3. The activation energy of the contact noise rate constant in the amalgam electrode system is 0.5 eV, which is close to that associated with bulk current noise in Naβ"alumina.

4. The contact noise is attributed to the interactions between the sodium species at the electrolyte-electrode interface.

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* On leave from Shanghai Institute of Ceramics, Chinese Academy of Science.

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Table 1. Noise decay parameters of contacts to Naβ"alumina

Concentration Mole % Na	Frequency Hz	Pre-exponential Factor A (v^2/Hz)	Rate Constant, k 10^{-3} Sec^{-1}
Sodium amalgam			
0.19	10	3.52×10^{-12}	0.702
1.24	10	1.02×10^{-12}	1.38
2.34	10	6.82×10^{-13}	1.71
4.96	10	9.79×10^{-14}	3.16
NaI propylene carbonate solution			
0.4	1	2.22×10^{-14}	0.277
	0.1	3.62×10^{-12}	0.282
4.2	1	1.46×10^{-14}	0.328
	0.1	1.52×10^{-12}	0.332
8.6	1	1.70×10^{-14}	0.448
	0.1	3.35×10^{-13}	0.460

FIGURE CAPTIONS

Figure 1. Contact noise spectra for sodium amalgam and NaI propylene carbonate solution to Naβ"alumina ceramics. The times shown are the ageing times after contact preparation.

Figure 2. Typical noise decay data and calculated curves from Equation (1).

Figure 3. Rate constant vs sodium concentration in electrodes.

Figure 4. Temperature dependence of the reaction rate constant and prefactor A for the 1.24 mole% amalgam contact to Naβ"alumina.

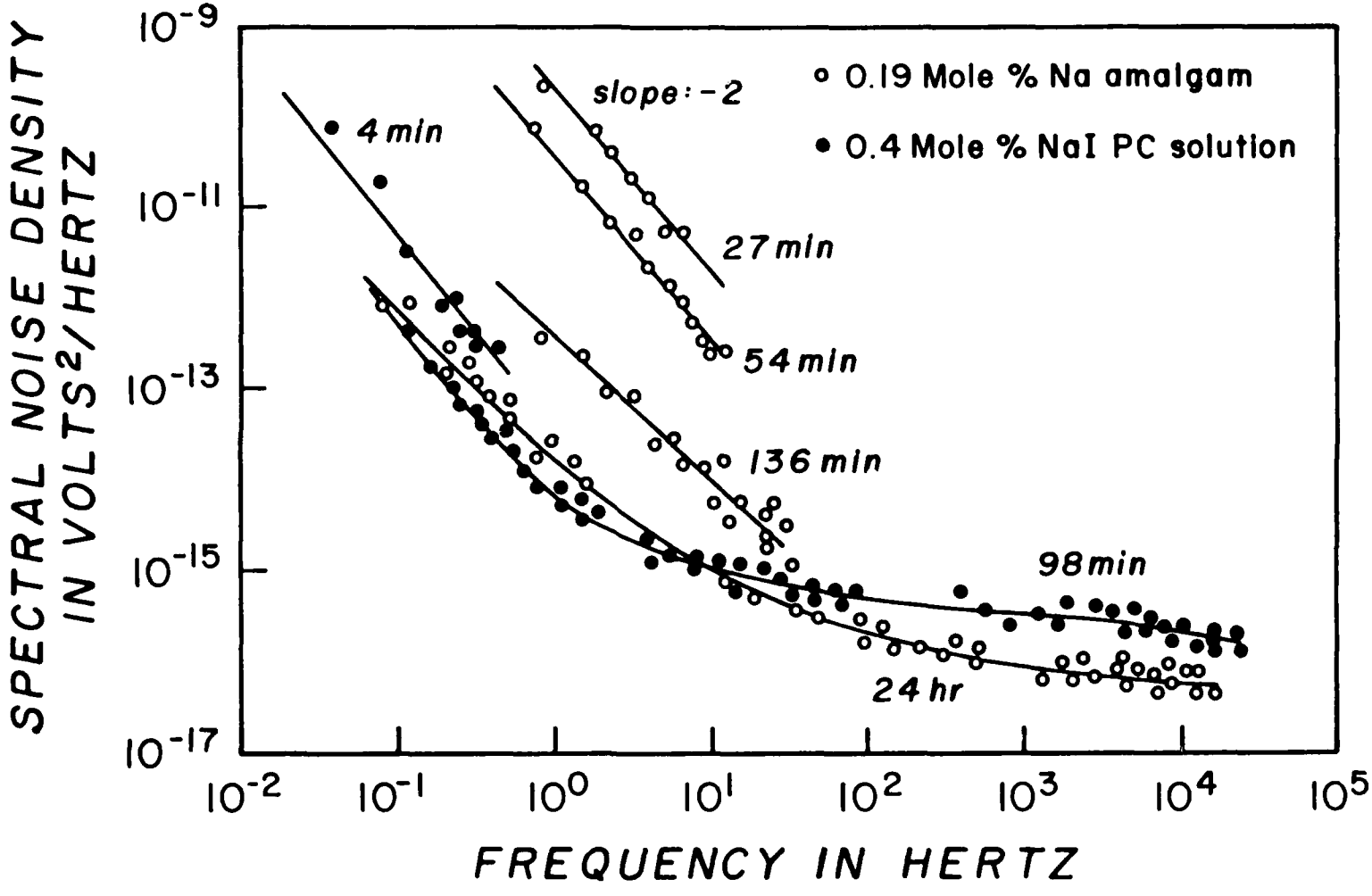
SPECTRAL NOISE DENSITY IN VOLTS²/HERTZ
FREQUENCY IN HERTZ
10⁻⁹
10⁻¹¹
10⁻¹³
10⁻¹⁵
10⁻¹⁷
10⁻²
10⁻¹
10⁰
10¹
10²
10³
10⁴
10⁵
slope: -2
o 0.19 Mole % Na amalgam
• 0.4 Mole % NaI PC solution
4 min
27 min
54 min
136 min
98 min
24 hr

Figure 1

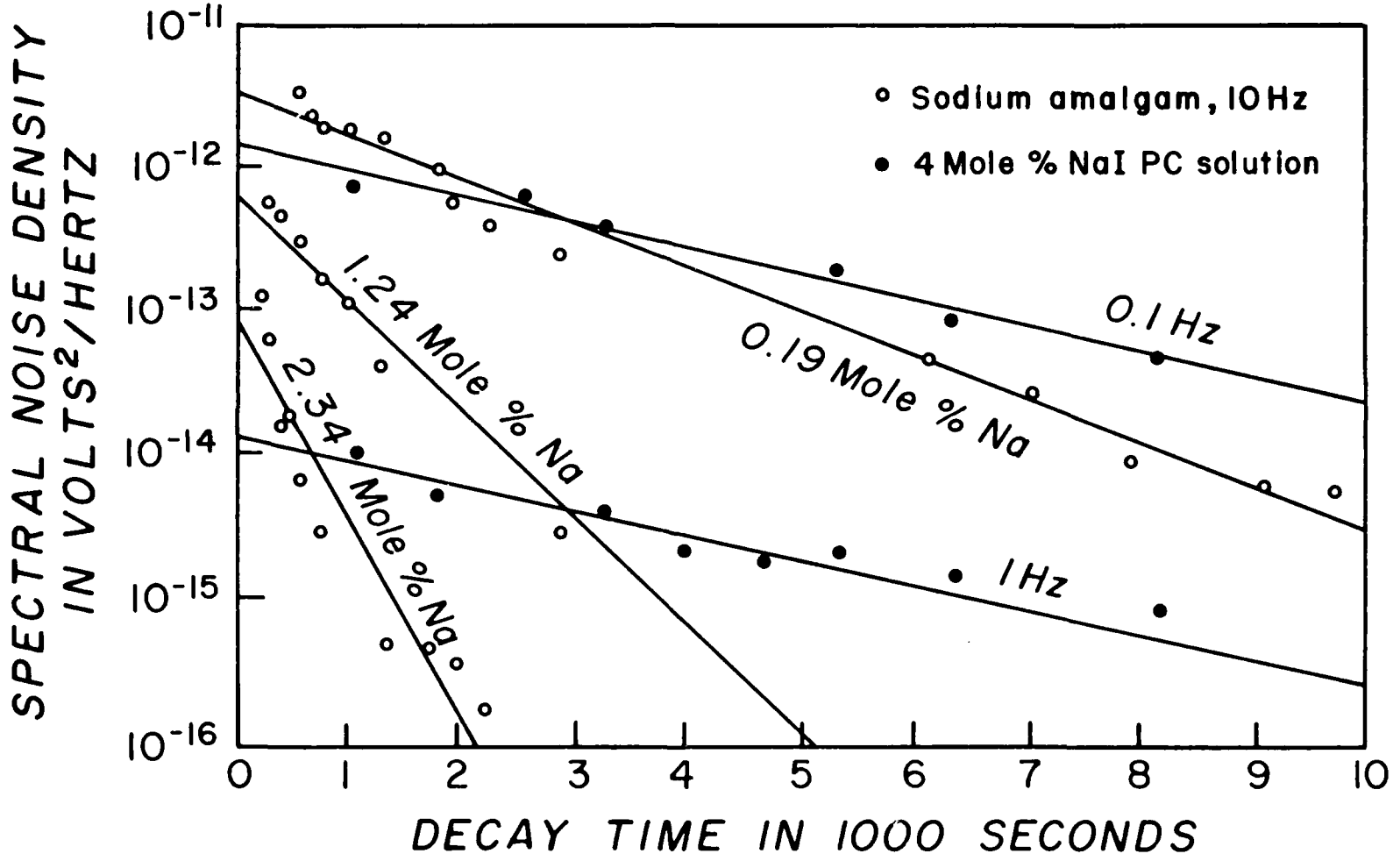
SPECTRAL NOISE DENSITY IN VOLTS²/HERTZ
10⁻¹¹
10⁻¹²
10⁻¹³
10⁻¹⁴
10⁻¹⁵
10⁻¹⁶
0
1
2
3
4
5
6
7
8
9
10
DECAY TIME IN 1000 SECONDS
Sodium amalgam, 10 Hz
4 Mole % NaI PC solution
0.1 Hz
0.19 Mole % Na
1.24 Mole % Na
2.34 Mole % Na
1 Hz

Figure 2

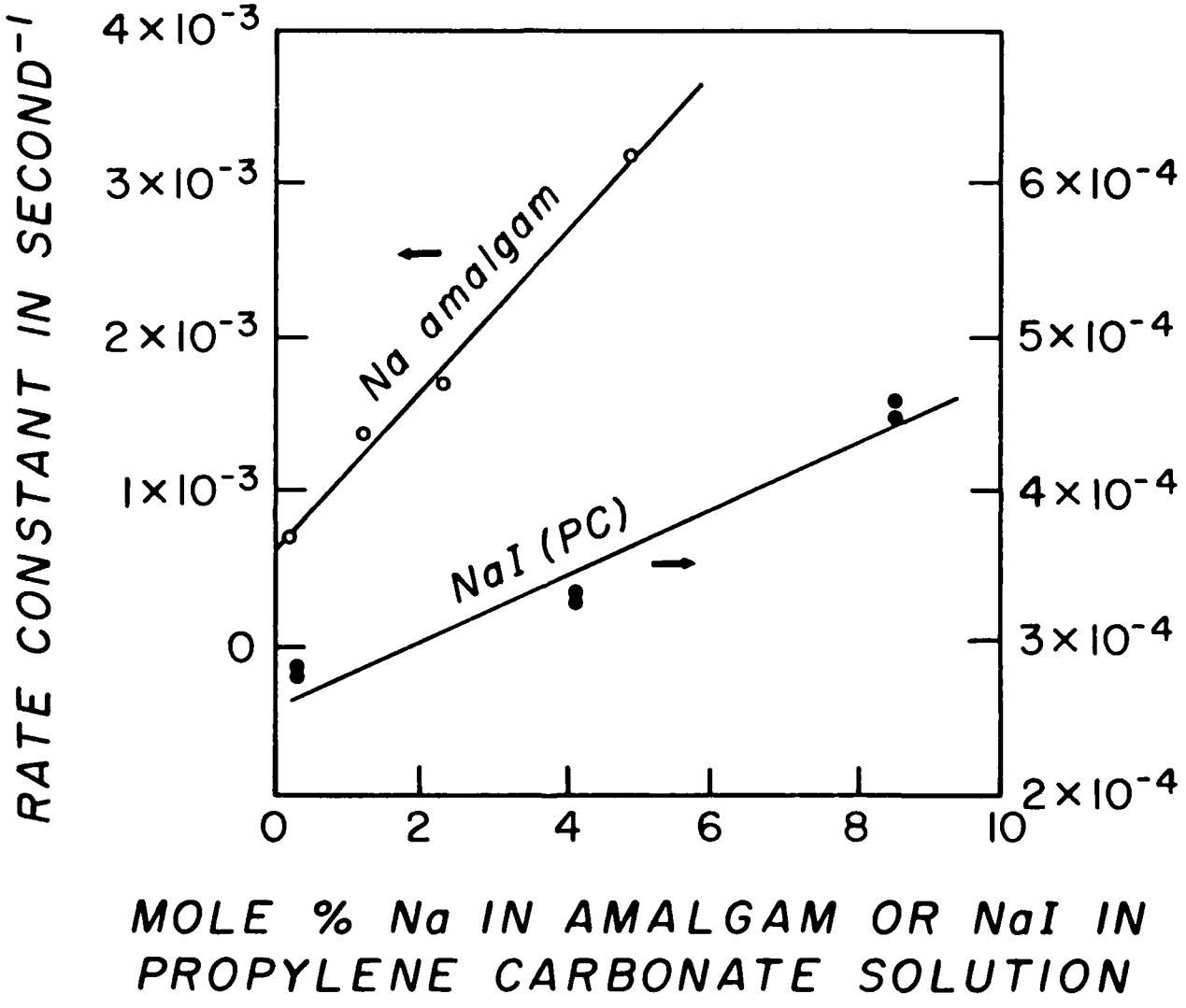
RATE CONSTANT IN SECOND⁻¹
4×10⁻³
3×10⁻³
2×10⁻³
1×10⁻³
0
6×10⁻⁴
5×10⁻⁴
4×10⁻⁴
3×10⁻⁴
2×10⁻⁴
Na amalgam
NaI (PC)
0
2
4
6
8
10
MOLE % Na IN AMALGAM OR NaI IN PROPYLENE CARBONATE SOLUTION

Figure 3

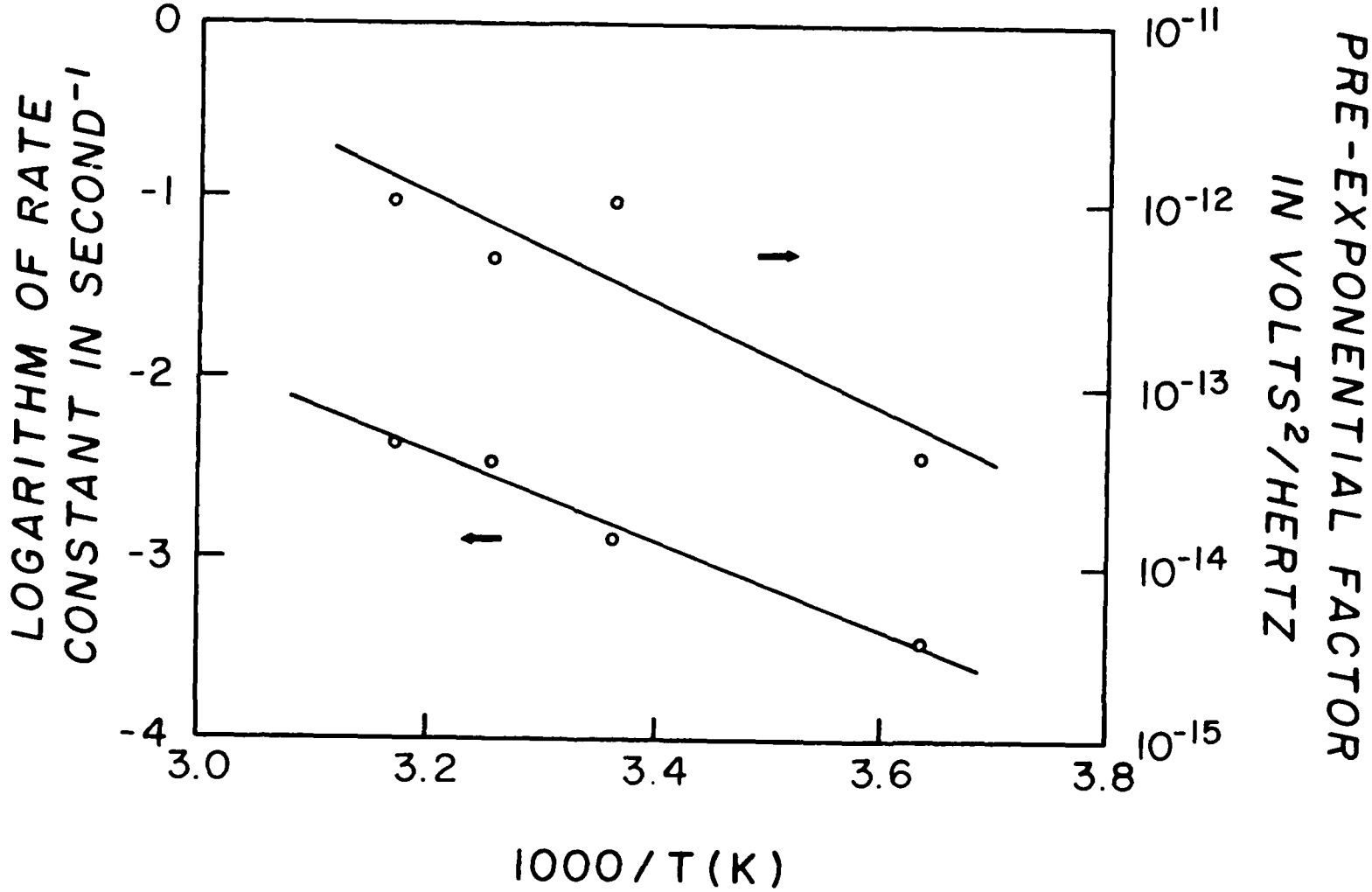
LOGARITHM OF RATE CONSTANT IN SECOND⁻¹
0
-1
-2
-3
-4
PRE-EXPONENTIAL FACTOR IN VOLTS²/HERTZ
10⁻¹¹
10⁻¹²
10⁻¹³
10⁻¹⁴
10⁻¹⁵
3.0
3.2
3.4
3.6
3.8
1000/T(K)

Figure 4

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