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CONCENTRATION-INTENSITY RELATIONSHIPS IN ELECTROGENERATED CHEMILUMINESCENCE

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ABSTRACT

Analytical applications of electrochemiluminescence are described. The peak intensity of luminescence, generated by application of an alternating current to solutions of 9,10-diphenylanthracene, varies linearly with concentration over the range 0.2 - 10 mM.

INTRODUCTION

There have been numerous reports during the past years of emission of light from solutions undergoing electrolysis. This type of chemiluminescence usually resulted from the formation of oxygen at the anode in aqueous solutions, followed by the usual type of chemiluminescent reaction involving oxygen.[1]

More recently, several workers have observed a new type of electrochemiluminescence (ECL) resulting from the electrolysis of various polycyclic aromatic hydrocarbons dissolved in deoxygenated nonaqueous solvents.[2-6] The emission appears to be from an excited, usually singlet, state of the hydrocarbon and the light reaction occurs in solution, not at the surface of the electrode.

Most of the reports have been concerned, not with analytical application of ECL, but with observations of the phenomenon itself and with proposed mechanisms. Feldberg[7] has derived, using computer techniques, theoretical equations relating, quantitatively, the light intensity produced in ECL to the current, time, and kinetic parameters using a double potential step mode of generation. The purpose of this paper is to describe some preliminary **experiments** we have performed which suggest possible analytical **applications** of ECL.

EXPERIMENTAL

9,10-Diphenylanthracene (DPA) was vacuum sublimed at ca. 200°C. Polarographic grade tetra-n-butylammonium perchlorate (TBAP) was vacuum dried at 85°C. for 24 hours and used as the supporting electrolyte. Solvent grade N,N-dimethylformamide (DMF) was dried over anhydrous $CuSO_4$ for 48 hours and distilled prior to use.

A rather simple apparatus was employed, so that a practical method might be developed without resorting to a complicated electrochemical cell or circuit design. The cell used in this experiment is shown in Figure 1, and consisted of two
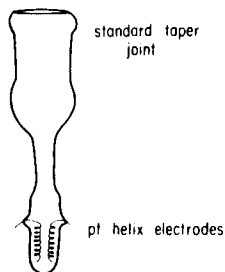
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coiled platinum electrodes sealed into the walls of a standard-taper joint. The power supply was a 6.3 V AC source. Portions of the alternating sinusoidal voltage were applied directly to the cell using a Variac transformer as a voltage divider.

A stock solution of 10 m$\underline{M}$ DPA in DMF was prepared and portions of it were diluted to make up solutions of different concentrations. Solutions of DPA between 1 m$\underline{M}$ and 0.1 m$\underline{M}$ were 0.1 $\underline{M}$ in supporting electrolyte (TBAP), while the more concentrated DPA solutions were 1 $\underline{M}$ in TBAP to decrease the solution resistance and to ensure that mass transfer of ions was predominantly by diffusion. The upper limit of concentration of DPA investigated was governed by the solubility limit of DPA in DMF (ca. 10 m$\underline{M}$); at DPA concentrations less than 0.2 m$\underline{M}$ the light intensity was too small to be accurately measured. All solutions were vacuum degassed and sealed off prior to carrying out the intensity measurements.

The cell was placed, in a reproducible fashion, inside the spectrophotofluorometer (Aminco-Bowman), and the emission spectrum recorded (Moseley model 2D-2 X-Y recorder) upon the passage of an alternating current between the two electrodes. All intensity-time curves were recorded at an emission wavelength of 429 mμ, the wavelength of maximum emission for DPA.

The experimental procedure consisted of recording the intensity-time behavior for each voltage, stirring the solution, and waiting two minutes before recording another curve. The relative intensity for each concentration was measured as an average of at least three experimental trials.

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RESULTS

A typical intensity-time (I-t) curve resulting from the
application of an alternating current to the cell is shown
in Figure 2. Zero time corresponds to the moment the current
is switched on, i.e., the initial intensity spike begins at
zero time. The intensity goes through a peak value and then
decays to a steady-state value; a plot of I vs. $t^{\frac{1}{2}}$ on the
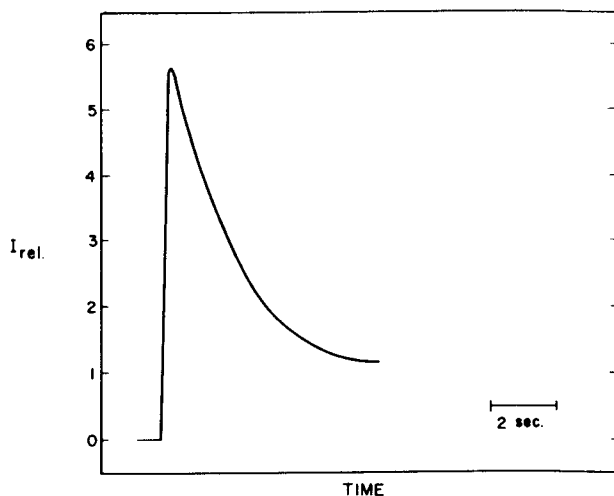decaying portion is linear.

FIG. 2

Plot of intensity (in arbitrary units) vs. time in the 9,
10-diphenylanthracene (DPA) system.

The effect of varying the magnitude of the alternating
voltage is shown in Figure 3. As the magnitude of the voltage
was increased, the peak intensity increased until, finally,
a constant "limiting" value was obtained. This probably cor-
responds to the application of a potential sweep of sufficient
magnitude to cause the potential to step to the limiting cur-
rent region of the current-potential curves.

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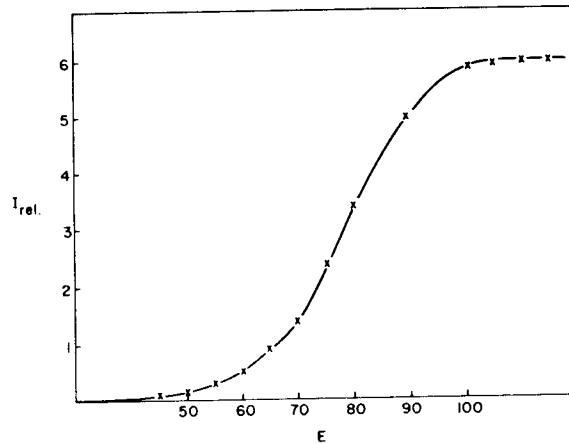
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FIG. 3

Intensity of light emission (in arbitrary units) <u>vs</u>. applied
a.c. voltage. The solution contained 0.1 M tetra-n-butyl
ammonium perchlorate and 9,10 DPA in DMF.

A plot of peak intensity <u>vs</u>. concentration is shown in

Figure 4; log-log coordinates were chosen to include the whole

concentration range. The voltage was adjusted to the limiting

region value for each concentration. As can be seen, the peak

intensity varied linearly with the concentration.

CONCLUSIONS

That the peak intensity is a linear function of the

concentration, suggests that this form of emission spectro-

scopy could find application as an analytical technique. There

are, of course, many limitations to this technique, such as

the effect of mixtures of chemiluminescent materials, the

variable effect of quenchers and impurities, and the fairly

specific nature of the phenomenon. Experiments are in progress

to investigate these effects and to discover further
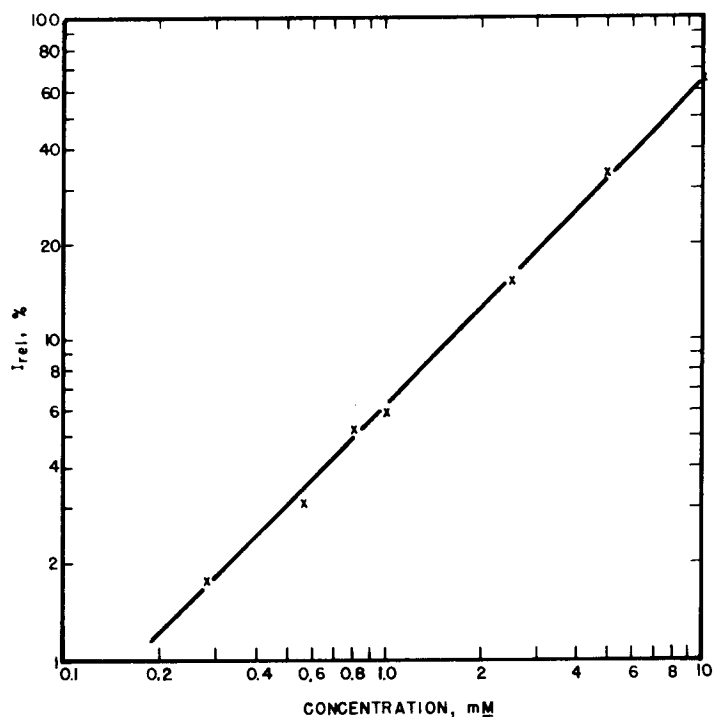
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FIG. 4

Intensity of light emission (in arbitrary units) obtained at different concentrations of 9,10-diphenylanthracene.

ACKNOWLEDGEMENTS

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