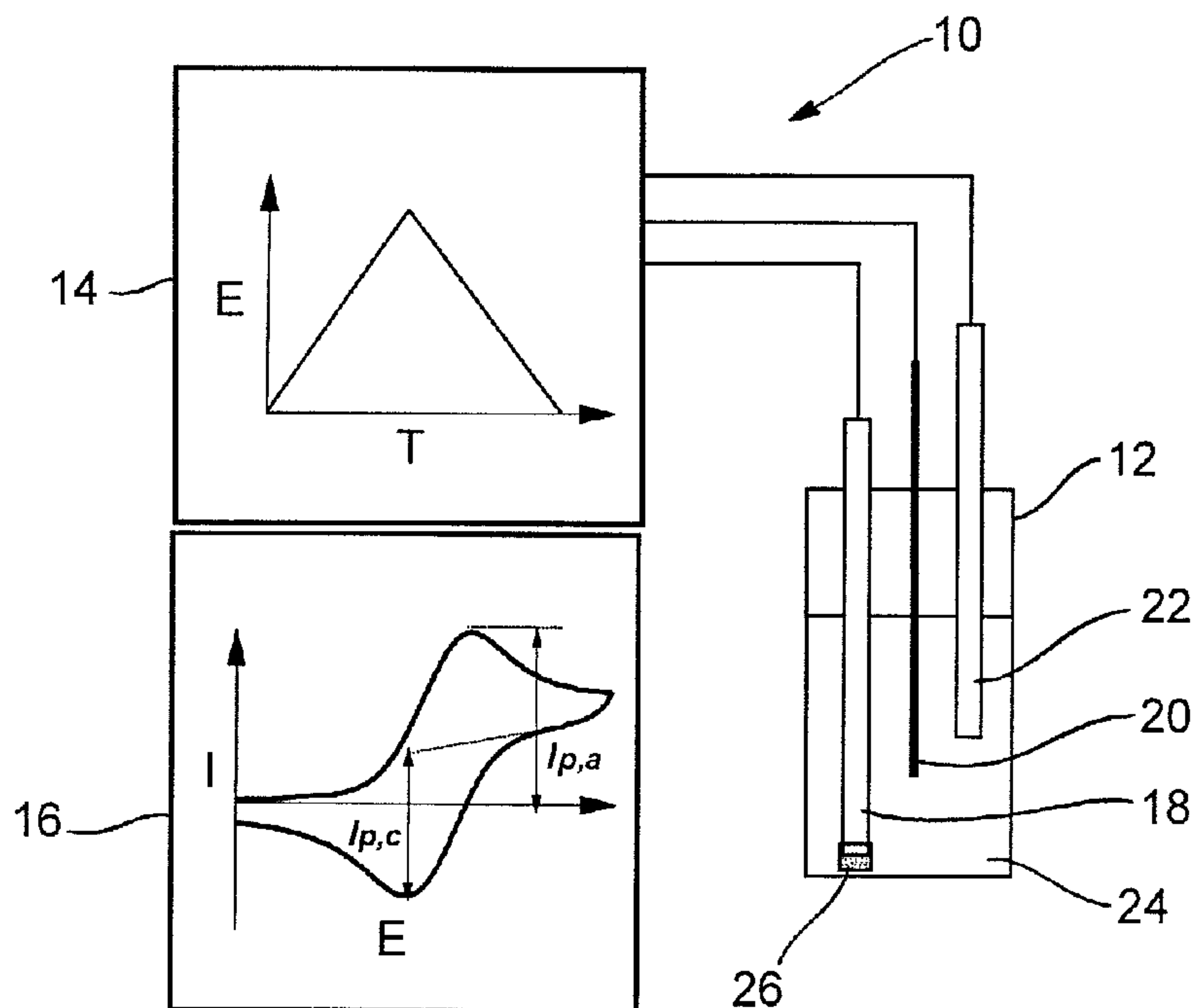




(22) Date de dépôt/Filing Date: 1999/12/23
(41) Mise à la disp. pub./Open to Public Insp.: 2001/06/23
(45) Date de délivrance/Issue Date: 2004/02/10

(51) Cl.Int.⁷/Int.Cl.⁷ G01N 27/49, D21C 7/12
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(54) Titre : METHODE ELECTROCHIMIQUE POUR DETERMINER LA TENEUR EN LIGNINE D'UNE PATE A PAPIER
(54) Title: ELECTROCHEMICAL METHOD FOR DETERMINATING LIGNIN CONTENT OF PULP



(57) **Abrégé/Abstract:**

This invention describes a new method to measure kappa number or lignin content of kraft pulps based on the voltammetric measurement of catalytic reactions involving lignin and redox mediators. This method comprises measuring the rate of regeneration of a lignin redox catalyst in the presence of pulp following its oxidation at a voltammetric electrode. The intensity of the catalytic current generated at the electrode surface is shown to be proportional to the amount of lignin present in a pulp. Within pulp types (softwood, hardwood or oxygen delignified) linear relationships can be obtained between the intensities of the generated current and a range of kappa numbers. The redox characteristics and concentration of the mediator, and the voltage sweep rate of the voltammetric procedure, are among parameters that can be tuned to obtained linear relationships with kappa number of various pulps. Automation of this method can lead to development of a novel on-line electro-kappa analyzer to be used for either pulping or bleaching process control.

Abstract

This invention describes a new method to measure kappa number or lignin content of kraft pulps based on the voltammetric measurement of catalytic reactions involving lignin and redox mediators. This method
5 comprises measuring the rate of regeneration of a lignin redox catalyst in the presence of pulp following its oxidation at a voltammetric electrode. The intensity of the catalytic current generated at the electrode surface is shown to be proportional to the amount of lignin present in a pulp. Within
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ELECTROCHEMICAL METHOD FOR DETERMINATING LIGNIN CONTENT OF PULP

TECHNICAL FIELD

The present invention relates in general to the pulp and paper industry, and in particular, to a new electrochemical method to measure lignin content and/or kappa number of wood pulps and pulping and bleaching spent liquors.

BACKGROUND ART

10 In order to produce a high and uniform quality kraft pulp, it is necessary to efficiently control the pulping and bleaching processes. The measurement of pulp kappa number is commonly used to monitor and control cooking conditions, and to estimate the amount of bleaching chemicals that should be added to obtain the target pulp brightness without chemical waste.

15 Furthermore, mills using an oxygen delignification stage also require reliable measurements of kappa number to prevent excessive delignification and fibre degradation. Manual measurement of kappa number using the standard sodium permanganate titration method takes several hours. The delay between kappa measurement and process

20 modification is not compatible with an efficient process control strategy which requires uninterrupted monitoring of pulp quality. Automatic on-line kappa analyzers are able to measure kappa number within a few minutes, so that changes in the process can be handled quickly. Several automated kappa analyzer systems have been developed for commercial

25 application. They all measure optical properties of pulp fibre suspensions. UV light absorption is used in the "Opti-Kappa Analyser" developed by STFI (Kubulnieks *et al.*, Tappi J., November 1987, pp. 38-42) while other systems which operate on a similar principle use the reflection of UV light

instead of absorption. These were developed by BTG Inc. (Agnéus and Damlin, Proceedings of the 24th Eucepa Conference, Stockholm, Sweden, 1990, pp. 234-241) , Valmet Automation Kajaani Inc. (Ollila and Erkkilä, TAPPI Proceedings of the 1997 Process & Product Quality Conference & Trade Fair, Jacksonville, Fl., pp. 117-122) and Honeywell-Measurex (Van Fleet and Whalley, TAPPI Proceedings of the 1998 Pulping Conference, pp. 1509-1512) and US Patent No. 5,953,111. Fluorescence measurement (Berthold *et al.*, U.S. Pat. Nos. 5,216,483 and 5,220, 172) and color shift of fluorescence (Jeffers and Malito, U.S. Pat. No. 5,486, 915) were applied to measure lignin content in wood pulp. In general, the optical based measurement systems are very sensitive to pulp consistency variation. Thus, in order to obtain an accurate lignin measurement, a strict control of the pulp consistency is also required.

Electrochemical sensors are commonly used in a vast range of applications, such as environmental monitoring, industrial quality control, and biomedical analysis. In the pulp and paper industry, amperometric/polarographic and potentiometric sensors are used to measure concentration of various oxidizing or reducing chemicals in pulping and bleaching liquors. Thus, polarographic methods can selectively and quantitatively measure sulfide, sulfite, thiosulfite and sulfhydryl compounds in kraft liquors (Noel, Tappi J. 61(5): 73-76, 1978) and chlorine dioxide and chlorite in bleach spent liquors (Willems and Williamson, In: Dence, C.W. and Reeve, D.W., eds. Pulp Bleaching - Principles and Practice, Tappi Press, 1996, pp. 625-645). However, these sensors are not able to measure lignin in fibre, because a close contact between lignin and the surface of the electrode is needed in order to permit free electron flow. Recent developments in the field of enzymatic bleaching of kraft pulp have shown that the enzyme laccase can delignify kraft pulp and oxidize lignin

model compounds when a redox mediator is present (Bourbonnais and Paice, FEBS Lett 267:99-102, 1990 and Appl. Microbiol. Biotechnol. 36:823-827, 1992). The redox mediator acts as a diffusible electron carrier between residual lignin in the fibre wall and the large laccase molecule in solution. Electrochemical studies of the interaction between lignin and the redox mediators have shown that the electrochemically oxidized mediator is continuously regenerated at the electrode surface following its reduction by lignin model compounds (Bourbonnais *et al.*, Biochim. Biophys. Acta. 1379:381-390, 1998). The kinetics of the redox reaction was shown to be related to the concentration of the lignin model compound.

The purpose of the present invention is to apply voltammetric methods to a pulp suspension, in the presence of a soluble lignin redox mediator, for quantitative and rapid measurement of kraft pulp lignin content.

15 DISCLOSURE OF THE INVENTION

This invention provides a new method to measure kappa number or lignin content of kraft pulps based on the voltammetric measurement of catalytic reactions involving lignin and redox mediators. This electrochemical method comprises measuring the rate of regeneration of a lignin redox catalyst in the presence of pulp following its oxidation at a voltammetric electrode. The intensity of the catalytic current generated at the electrode surface is proportional to the amount and oxidation state of lignin present in the pulp. Linear relations between kappa numbers and the intensities of the generated current can be obtained within various ranges of kappa numbers and types of pulp. The redox characteristics and concentration of the mediator, and the voltage sweep rate of the voltammetric procedure are parameters that can be tuned to obtained linear relations with various pulps.

In accordance with one aspect of the invention there is provided a method of determining kappa number or lignin content of a pulp comprising: i) contacting a sample of the pulp with a voltammetric electrode in an electrochemical cell, in the presence of a redox mediator effective in an oxidized state effective to oxidize lignin in the pulp, with formation of a reduced state of said redox mediator and a current discharge at said electrode which re-oxidizes the redox mediator; ii) measuring the peak intensity of the current discharge voltammetrically at said electrode, and iii) determining the kappa number or lignin content of the pulp sample from the measured peak intensity in ii).

In another aspect of the invention there is provided a method for analyzing the lignin content of a pulp comprising: a) mixing a sample of the pulp with a redox mediator; b) placing the resulting sample in contact with a working electrode in a cyclic voltammetry apparatus, c) measuring the intensity of the peak current generated at the electrode, and d) converting the peak current to kappa number from calibration data determined with pulps of known lignin content.

BRIEF DESCRIPTION OF DRAWINGS

Fig. 1 illustrates schematically the measurement of pulp kappa number by cyclic voltammetry, in accordance with the invention;

Fig. 2 illustrates schematically a mediator coupled electrochemical method of the invention for determining pulp kappa number;

Figs 3a and 3b illustrate graphically cyclic voltammetry of a redox mediator ABTS alone (Fig. 3a) and in the presence of a kraft pulp (Fig. 3b);

Figs. 4a, 4b and 4c illustrate graphically the relationship between peak current intensities and kappa number, for different pulps;

Fig. 5 is a graphical illustration of the relationship between the

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kappa number of softwood oxygen delignified kraft pulps and the peak current intensities (I_k) of ABTS (0.2 mM);

Fig. 6 is a graphical illustration of the relationship between mixed hardwood kraft pulps and the peak current intensities (I_k) of ABTS (0.2 mM);

Fig. 7 is a graphical illustration of the relationship between the kappa number of partially bleached kraft pulps after chlorine dioxide and alkaline extraction stages ($D_{100}E$) and the peak current intensities (I_k) of ABTS (0.2 mM);

Fig. 8a illustrates graphically the cyclic voltammetry of a redox mediator, potassium octacyanomolybdate, in the presence of softwood kraft pulps;

Fig. 8b illustrates the linear relationship between pulp kappa number and peak current intensities (I_k);

Fig. 9 illustrates graphically the effect of pulp sample size on the ABTS peak current intensities; and

Fig. 10 illustrates graphically the relationship between peak current ratio ($I_{k, 520 \text{ mV}} / I_{k, 920 \text{ mV}}$) of ABTS and the type of pulp or extent of delignification.

20 DETAILED DESCRIPTION OF THE INVENTION AND DESCRIPTION OF PREFERRED EMBODIMENTS

The principle of this invention is based on the combination of an electroanalytical method such as cyclic voltammetry (CV) with the use of a soluble redox mediator catalyzing lignin oxidation.

As shown in Fig. 1, a basic voltammetry apparatus 10 includes an electrochemical cell 12, a potentiostat 14 and a recorder 16. Cell 12 has a

working electrode 18, an auxiliary electrode 20 and a reference electrode 22, a solution of a redox mediator 24 is housed in cell 12 and a sample 26 of pulp mixed with the mediator 24 is supported at the surface of working electrode 18. In use the potentiostat 14 simultaneously generates a linear potential scan at a working electrode 18, and measures the current resulting from the oxidation or reduction of the mediator 24 which is a redox active compound in the electrochemical cell 12.

The intensity of the peak current (I_p) measured at the surface of the working electrode 18, by recorder 16, is directly proportional to the concentration C of the target analyte, as shown by the Randles-Sevcik equation:

$$I_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} v^{1/2} C$$

where n is the number of electrons, A the area of the working electrode, D the diffusion coefficient of the analyte, and v the voltage scan rate.

This relationship applies to soluble redox couples, but cannot be used directly on lignin in pulp fibre, because there is no direct contact between lignin and the surface of the electrode. However, by addition of a soluble redox mediator, the electrode reaction can be efficiently coupled to lignin in pulp fibre. During the voltammetric process, the electro-oxidized mediator diffuses into the pulp fibre to react reversibly with lignin. The reaction with lignin regenerates the reduced mediator at the surface of the electrode, resulting in an increase of the current when compared to the mediator alone. Using a fixed concentration of mediator, the current measured at the peak potential of the mediator in the presence of pulp (I_k) is proportional to the amount of lignin or the kappa number of the pulp (see Figs. 2 and 3).

This invention can be applied to measure lignin content or kappa

number of hardwood or softwood kraft, or sulfite pulps, either during or after cooking and bleaching stages. The pulp is preferably washed with water or with the electrolyte buffer. After pressing or filtering, a fixed amount of pulp is mixed with a fixed amount of mediator 24 solution to form sample 26. For this purpose, a mediator can be any organic or inorganic compound which can form a redox couple at a potential between 0.3 to 1.2 volt when measured against an Ag/AgCl reference electrode (RE) 22. The pulp-mediator suspension sample 26 is applied and pressed at the surface of the working electrode (WE) 18 and soaked in electrochemical cell 12 containing the mediator solution 24, reference electrode (RE) 22 and the auxiliary (AE) electrode 20 (Fig. 1). Cyclic voltammetry determinations are carried out typically with a BAS CV-50W Voltammetric Analyser (Bioanalytical Systems, Inc., Indiana, USA) with an Ag/AgCl reference electrode 22, a platinum wire auxiliary electrode 20 and a 3mm diameter glassy carbon working electrode 18. Any combination of electrochemical cells 12, electrodes 18, 20, 22 and potentiostats 14 suitable for electrochemical analysis can also be used for this invention.

The redox mediator should suitably be reversible so that it can be repeatedly changed between the reduced and oxidized state. It is most convenient to employ redox mediators that are water soluble.

The range and the rate of voltage scans and peak potential measurements can be automatically performed by the voltammetric analyzer. By way of example, suitable mediators include 2,2'-azinobis(3-ethylbenzthiazoline-5-sulphonate) (ABTS) as organic mediator and potassium octacyanomolybdate [$K_4Mo(CN)_8$] as inorganic mediator. ABTS is available commercially and $K_4Mo(CN)_8 \cdot 2H_2O$ may be prepared according to Furman and Miller (Inorg. Synth. 3,160-163, 1950). The preferred organic mediator used to illustrate this invention is ABTS which

has two stable and reversible redox couples within a range of voltage potential suitable to oxidize lignin. The first anodic peak, appearing when the electrode potential reaches 0.52V, corresponds to the oxidation of ABTS to its cation radical ($\text{ABTS}^{\bullet+}$), whereas the second peak at 0.92V corresponds to the formation of the dication (ABTS^{2+}). Figure 3 shows cyclic voltammograms at a slow potential scan rate (2mV/s) with a) ABTS 0.2 mM in sodium citrate buffer, 0.1M, pH 4.5 and b) ABTS in the presence of softwood kraft pulp. The increase of the anodic current peak intensities of ABTS in the presence of pulps (I_k , catalytic current) when compared to ABTS alone (I_d , diffusion current) illustrates the extent of the reactions taking place between the two oxidized forms of ABTS and the residual lignin in kraft pulp. The intensity of the catalytic current at the peak potential of the mediator is proportional to the amount of residual lignin or the kappa number of the kraft pulp.

15

EXAMPLES

Example I

Electrochemical measurement of softwood kraft pulp kappa number with ABTS 0.5mM

20 Softwood kraft pulps with kappa number ranging from 32 to 87 were prepared by cooking eastern Canadian black spruce chips at various H factors in a pilot plant batch digester. Further delignification of black spruce kraft pulps was performed with a lab-scale oxygen pressurized reactor at various temperatures, reaction times and alkaline charges. The
25 softwood oxygen delignified pulps (SWO_2) obtained had kappa numbers ranging from 11 to 29. All pulp kappa number were measured by the permanganate titration method according to Tappi test procedure T236.

Cyclic voltammetry of pulps was performed as follows: After washing the pulp with water, a small sample (equivalent to about 10 mg of oven dried weight pulp) was suspended in 1mL solution of ABTS (0.5 mM) in sodium citrate (0.1M, pH 4.5). The pulp was then applied to the surface of the glassy carbon electrode by pressing the pulp against the bottom of the electrochemical cell. Cyclic voltammetry was performed at a scan rate of 2 mV/sec in an electrochemical cell containing a solution of ABTS 0.5 mM in citrate buffer, a platinum wire auxiliary electrode, a silver/silver chloride reference electrode, and the pulp sample fixed on the surface of the working carbon electrode. Current intensities (I_k) at the anodic peaks of ABTS/ABTS^{•+} (520 mV) and ABTS^{•+}/ABTS²⁺ (920 mV) were measured and plotted against kappa number of the pulp samples. Figures 4a-c show graphs of the variation of peak current intensities I_k of ABTS (0.5 mM) with the kappa number of softwood kraft pulps. In Figure 4a, where all softwood pulps from either kraft digester and oxygen stages are plotted together, the plot of I_k vs kappa number is not linear over the entire range of kappa number. However, when softwood pulps from the kraft digester (Figure 4b) and softwood pulps after O₂ stage delignification (Figure 4c) are plotted separately, a good linear correlation can be seen between I_k for both ABTS peak potentials and the kappa number of pulp samples. Error bars indicate the standard deviation of triplicates measurement.

Example 2

25 Effect of changing ABTS concentration

Oxygen delignified softwood kraft pulps were prepared and treated as described in the example 1, except that the concentration of ABTS used for electrochemical measurement was lowered to 0.2 mM . Voltammetric

determination were performed as described in the previous example. Figure 5 shows a good linearity between peak current of ABTS at 920 mV and the kappa number of all oxygen delignified pulps when ABTS is used at lower concentration. However, the curve describing the peak current intensities at 520 mV is less linear and seems to level off for more lower kappa pulps.

Example 3

Electrochemical measurement of hardwood kraft pulp kappa number

Mixed hardwood kraft pulp were prepared by cooking a mixture of maple, birch and aspen wood chips in pilot plant kraft digester to kappa number ranging from 16 to 21. Pulp samples were prepared as described in example 1, and cyclic voltammetry of pulp and ABTS 0.2 mM were run as described in example 2. As for softwood pulps, Figure 6 shows a linear relationship between both catalytic current intensities of ABTS and the kappa number of hardwood kraft pulps.

Example 4

Application of electro-kappa measurement for ECF bleaching sequences

Black spruce kraft pulp with a kappa number of 31.8, obtained from a pilot plant digester, was treated with chlorine dioxide (D₁₀₀ stage) followed by alkaline extraction (E stage). Various amounts of chlorine dioxide equivalent to active chlorine multiples (ACM) between 0.05 and 0.20 were applied to obtain partially bleached pulps with extracted kappa numbers ranging from 8 to 23.5. Pulp samples were prepared as described in example 1, and cyclic voltammetry of pulp and ABTS (0.2 mM) was performed as described in example 2. Results of linear regression curves of the catalytic current intensities at 520 and 920 mV versus the kappa number of these bleached pulps are shown in Figure 7.

Example 5

Use of inorganic redox mediator for electro-kappa measurement

In this example, potassium octacyanomolybdate was used as an inorganic redox mediator to measure kappa number of pulp samples. 5 Oxygen delignified softwood kraft pulps were prepared and treated as described in the example 1, except that ABTS was replaced by a solution of $K_4Mo(CN)_8$ (0.2mM) in sodium acetate buffer (0.1M, pH 4.5). This mediator has only one redox couple ($E^0 = 0.55V$) within the range of potential used to measure kappa number. Cyclic voltammograms of 10 octacyanomolybdate in the presence of kraft pulp at various kappa number are shown in Figure 8A, and the linear regression of the peak current intensities (I_k) versus kappa number of pulp samples is shown in Figure 8B.

Example 6

15 Effect of pulp sample size on the voltammetric response

In order to verify the importance of pulp sample size on the mediator peak current intensities, cyclic voltammetric experiments with ABTS (0.2 mM) were performed in the presence of various amounts of an oxygen-delignified softwood pulp ($\kappa = 21.4$). As shown in Figure 9, both 20 ABTS peak current intensities decrease only very slightly with the amount of pulp applied at the electrode surface. For pulp sample sizes between 8 to 12 mg, variations of I_k are within the standard deviation.

Example 7

Characterization of oxidation state of residual lignin

25 The peak current ratio for the two oxidation states ABTS (i.e. 520 and 920 mV) can be used as an indicator of the oxidation state of the residual lignin in the pulp. The increase of the peak current intensity at 520 mV

corresponds to the amount of more easily oxidable residues in lignin such as phenolic groups, whereas the increase of the current at 920 mV is more likely related to higher redox potential groups of lignin. Thus, a pulp with a high ratio of the peak current intensity at 520 mV over the one at 920 mV, indicates that the pulp can be more easily oxidized than a pulp having a lower peak ratio. This type of indication can lead to a more rational use and saving of bleaching chemicals. Figure 10 shows a graph of the peak current ratio of ABTS (0.2mM) ($I_{k, 520mV} / I_{k,920mV}$) in the presence of various pulps. A high ratio, such as in the case of hardwood kraft pulps, indicates that at the same kappa number, a hardwood kraft pulp is more easily oxidized or bleached than a softwood pulp. Furthermore, these results also indicate a difference in the oxidation state of a softwood kraft pulp when delignified to the same kappa number with chlorine dioxide followed by an extraction stage (DE) or with an oxygen stage (SWO₂).

CLAIMS

1. A method of determining kappa number or lignin content of a pulp comprising:
 - 5 i) contacting a sample of the pulp with a voltammetric electrode in an electrochemical cell, in the presence of a redox mediator, in an oxidized state effective to oxidize lignin in the pulp, with formation of a reduced state of said redox mediator and a current discharge at said electrode which re-oxidizes the redox mediator,
 - 10 ii) measuring the peak intensity of the current discharge voltammetrically at said electrode, and
 - iii) determining the kappa number or lignin content of the pulp sample from the measured peak intensity in ii).
2. A method according to claim 1, wherein said redox mediator is a
15 reversible redox mediator and forms a redox couple at a potential between 0.3 and 1.2 volts, when measured against an Ag/AgCl reference electrode.
3. A method according to claim 2, wherein said redox mediator is
20 water soluble.
4. A method according to claim 1, 2 or 3, wherein said redox mediator is 2,2'-azinobis(3-ethylbenzthiazoline-5-sulphonate).

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5. A method according to claim 1, 2 or 3, wherein said redox mediator is potassium octacyanomolybdate.
- 5 6. A method for analyzing the lignin content of a pulp comprising:
- a) mixing a sample of the pulp with a redox mediator
 - b) placing the resulting sample in contact with a working electrode in a cyclic voltammetry apparatus,
 - c) measuring the intensity of the peak current generated at the electrode,
 - 10 and
 - d) converting the peak current to kappa number from calibration data determined with pulps of known lignin content.
7. A method according to claim 6, where the redox mediator is an
- 15 organic or inorganic compound which can form a redox couple at a potential between 0.3 to 1.2 volt when measured against an Ag/AgCl reference electrode (RE).
8. A method according to claim 6 or 7, wherein said redox mediator is
- 20 water soluble and is a reversible redox mediator.
9. A method according to claim 6, 7 or 8, wherein the mediator is 2,2'-azinobis(3-ethylbenzthiazoline-5-sulphonate) (ABTS), and a ratio of two peak currents measured at 0.52 V and 0.92V is used to generate
- 25 information on the oxidation state of lignin in the pulp.
10. A method according to claim 6, 7 or 8, wherein said redox mediator is 2,2'-azinobis(3-ethylbenzthiazoline-5-sulphonate).

- 15 -

11. A method according to claim 6, 7 or 8, wherein said redox mediator is potassium octacyanomolybdate.

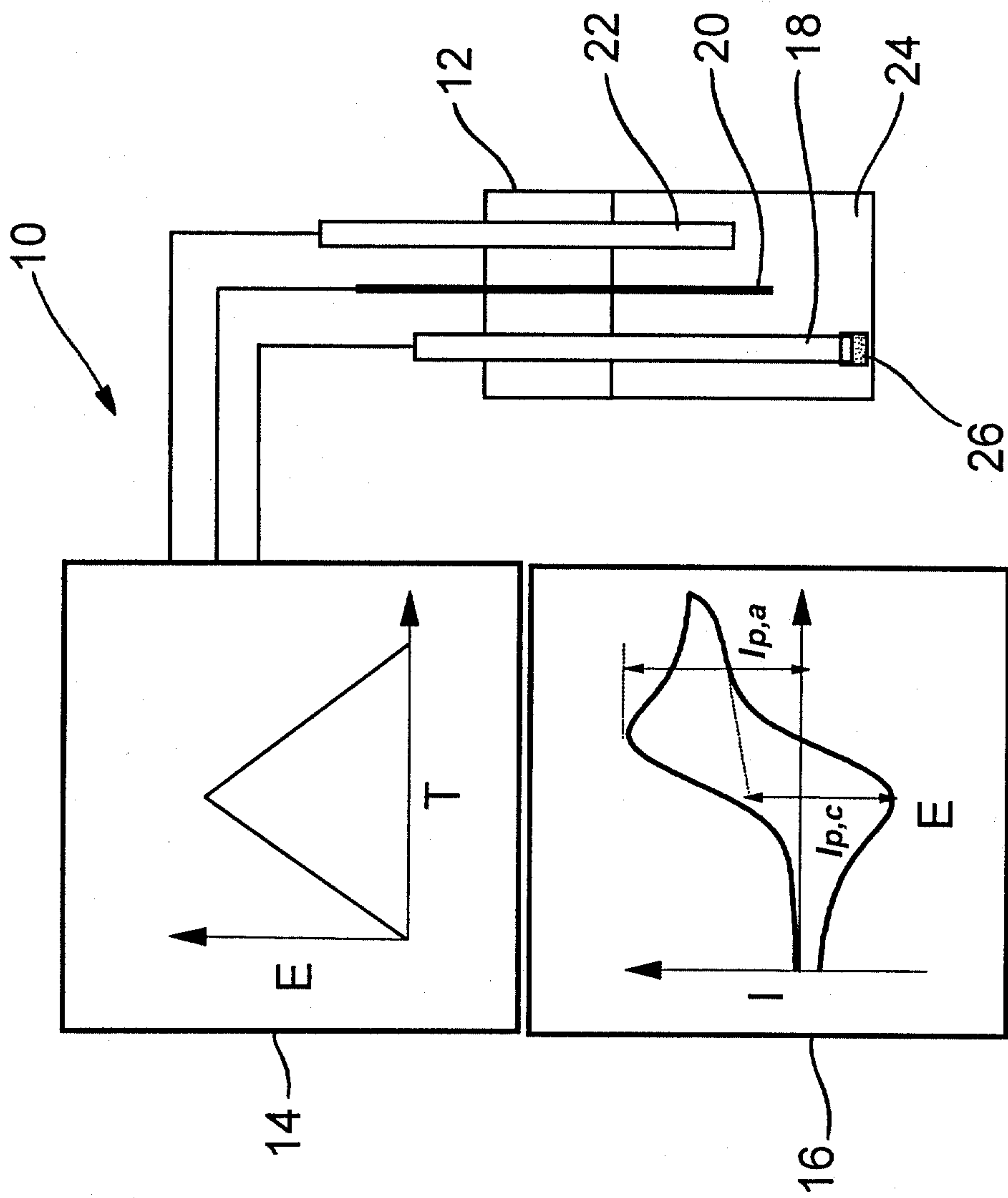
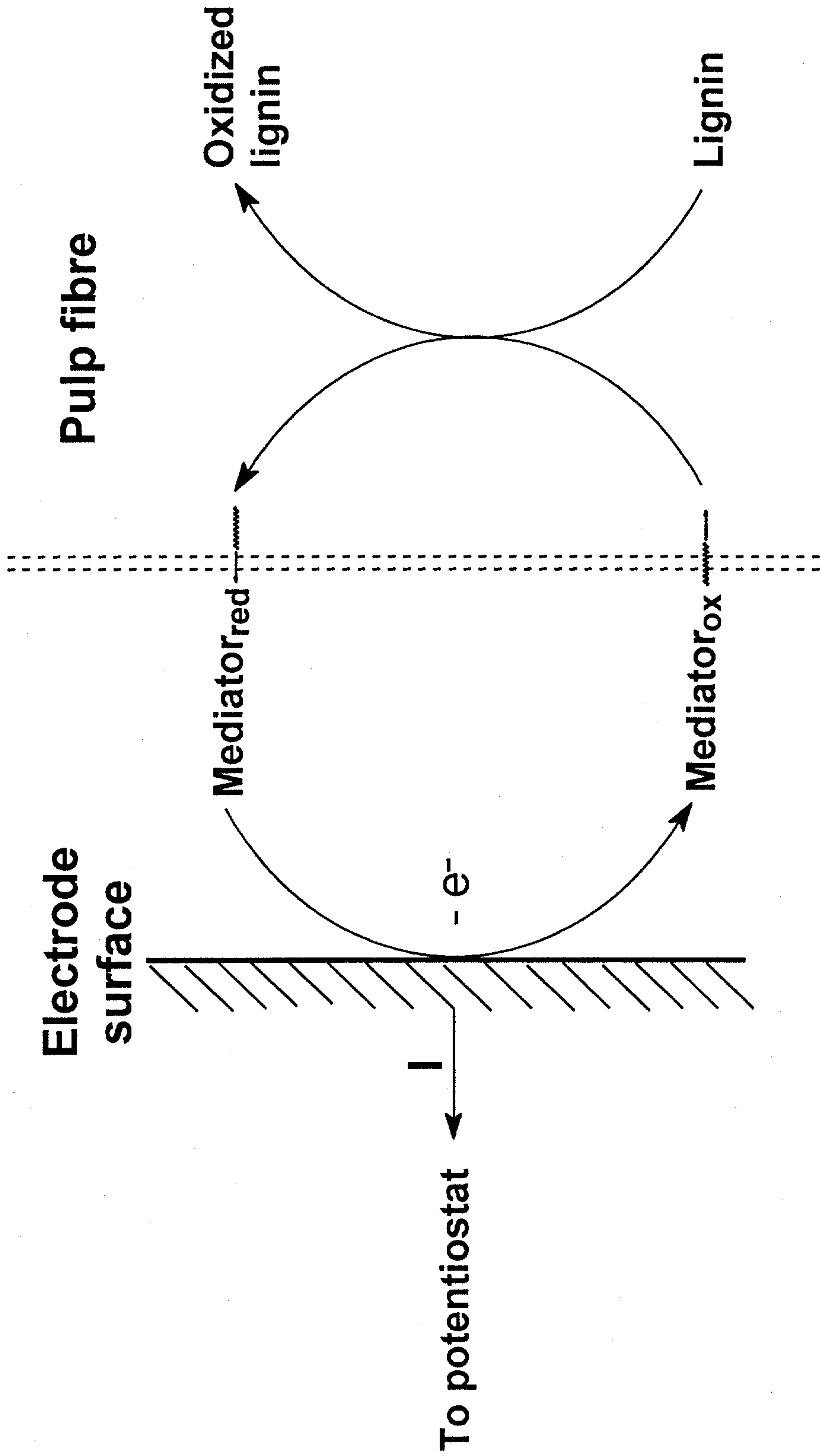
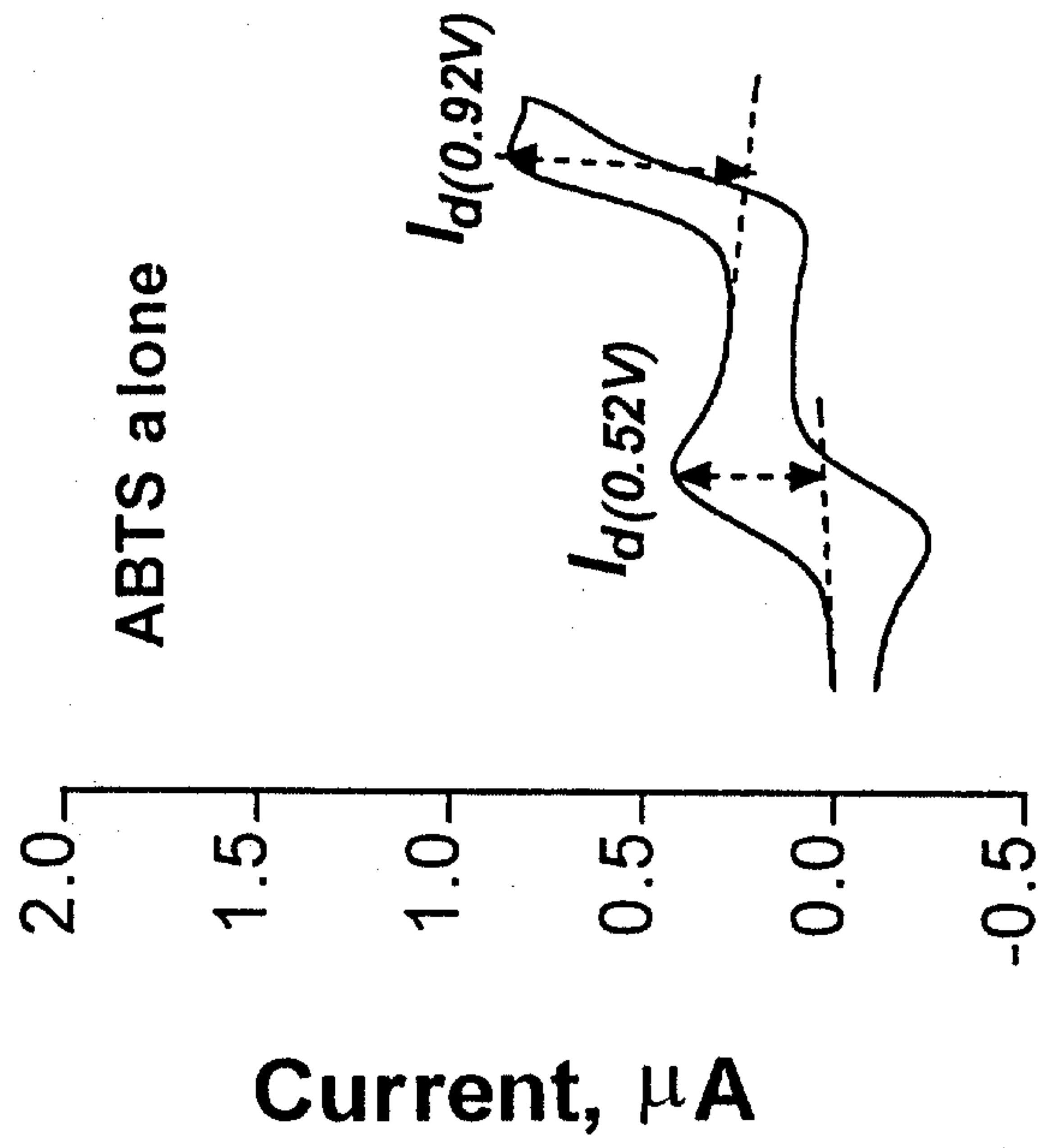
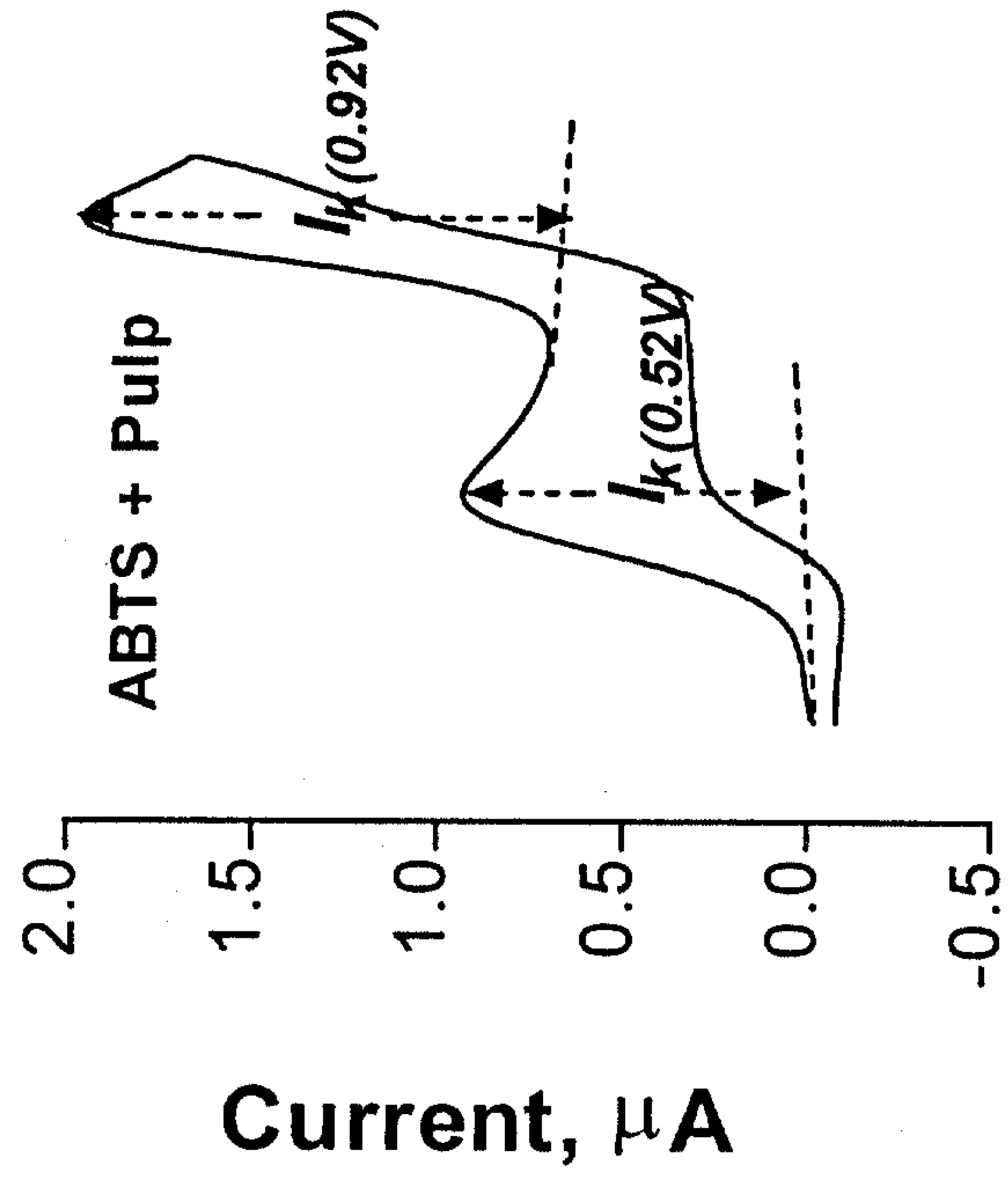
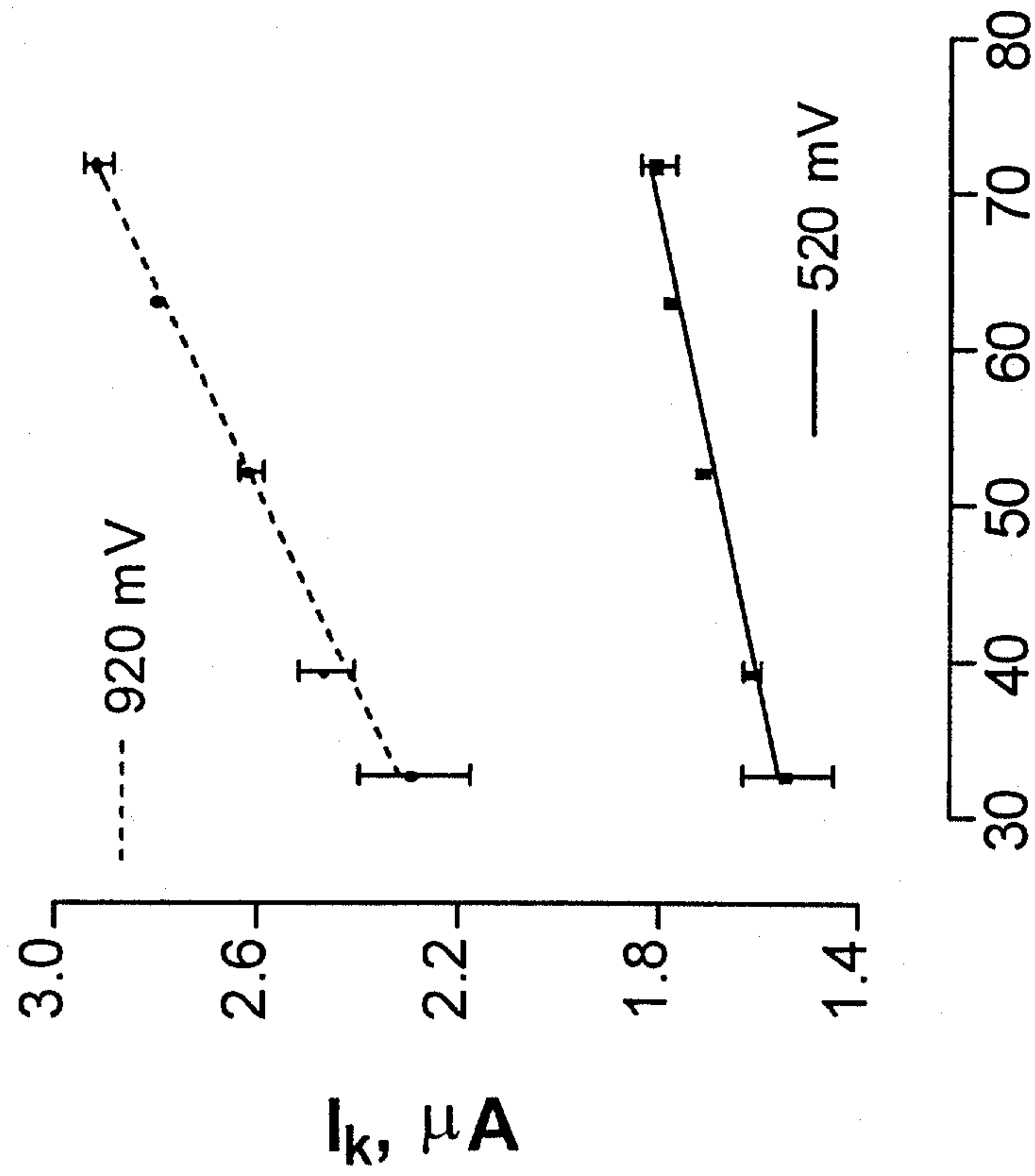


FIG. 1



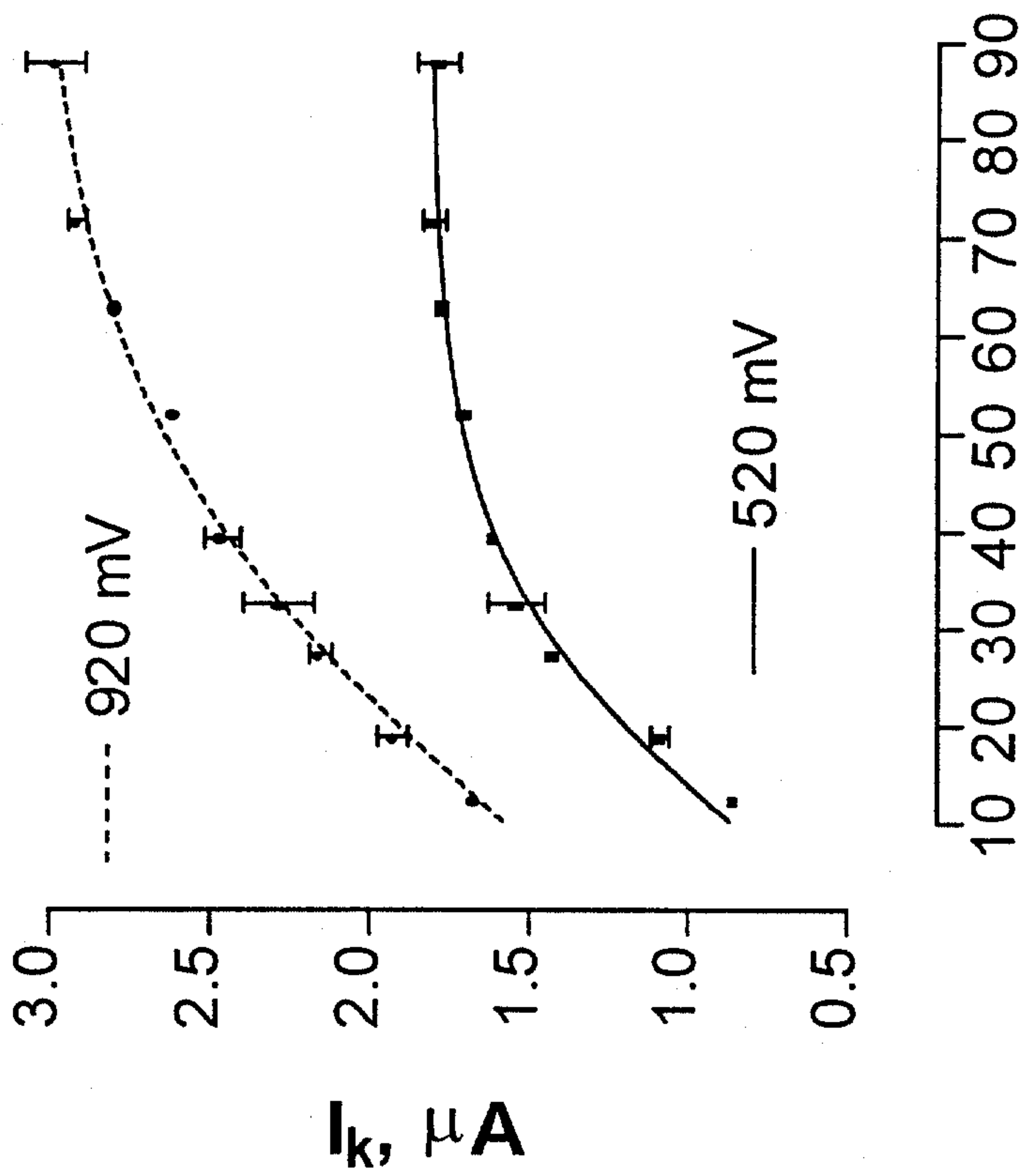
$I_k \propto \text{Reaction rate} \propto [\text{lignin}] \text{ or } \text{Kappa number}$





Kappa number

FEF-4b



Kappa number

FEF-4a

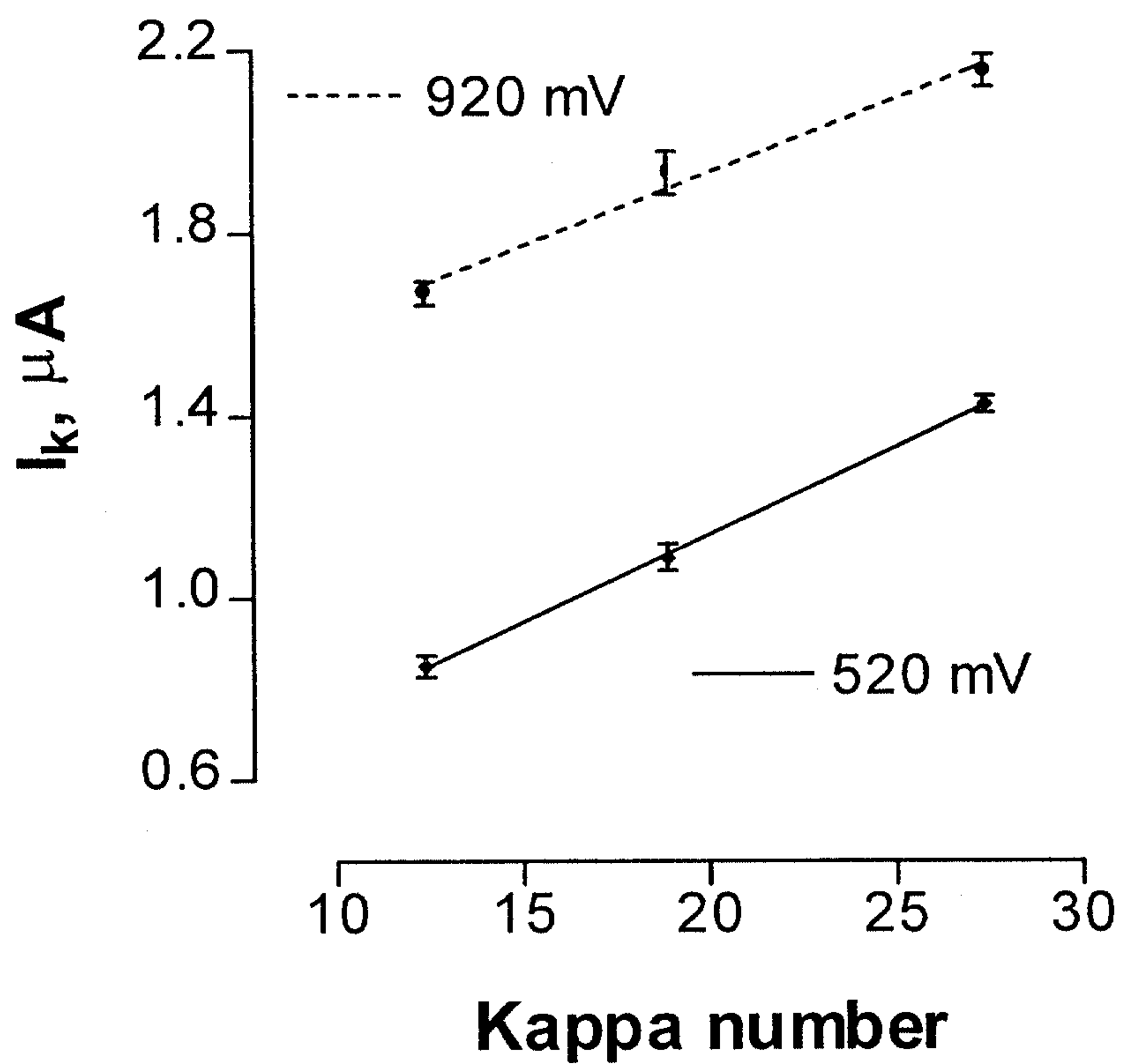
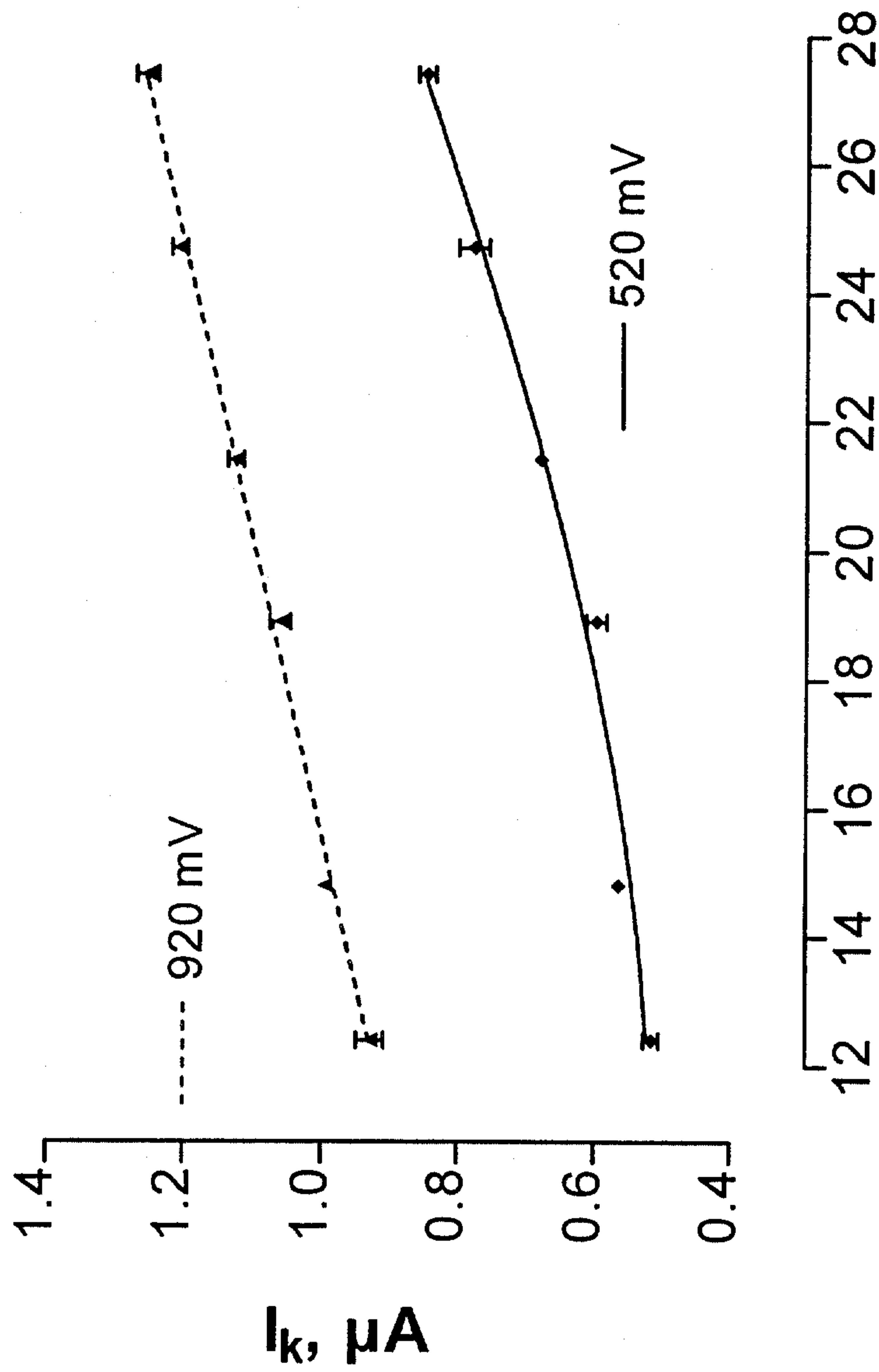
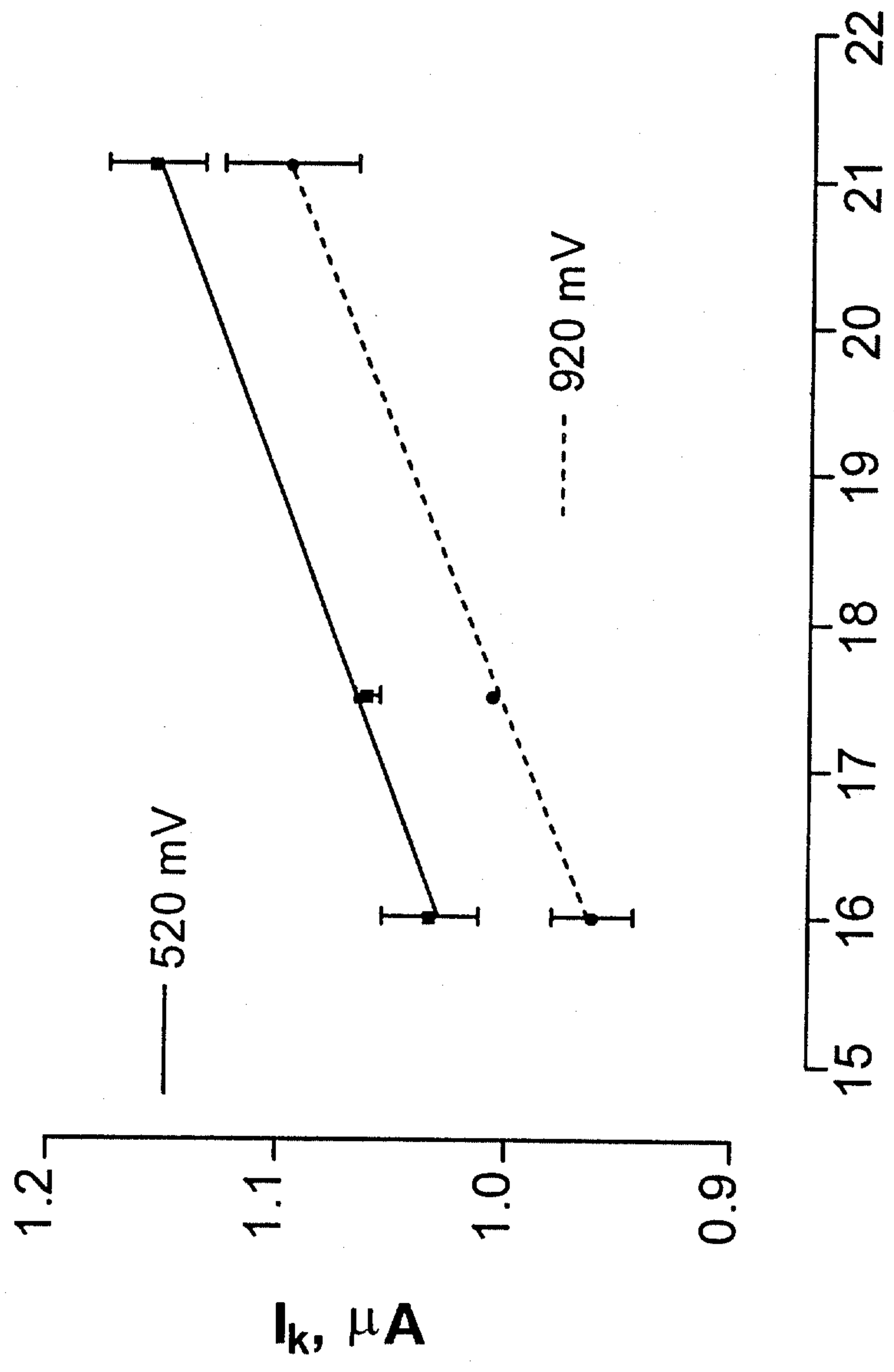


FIG - 4C



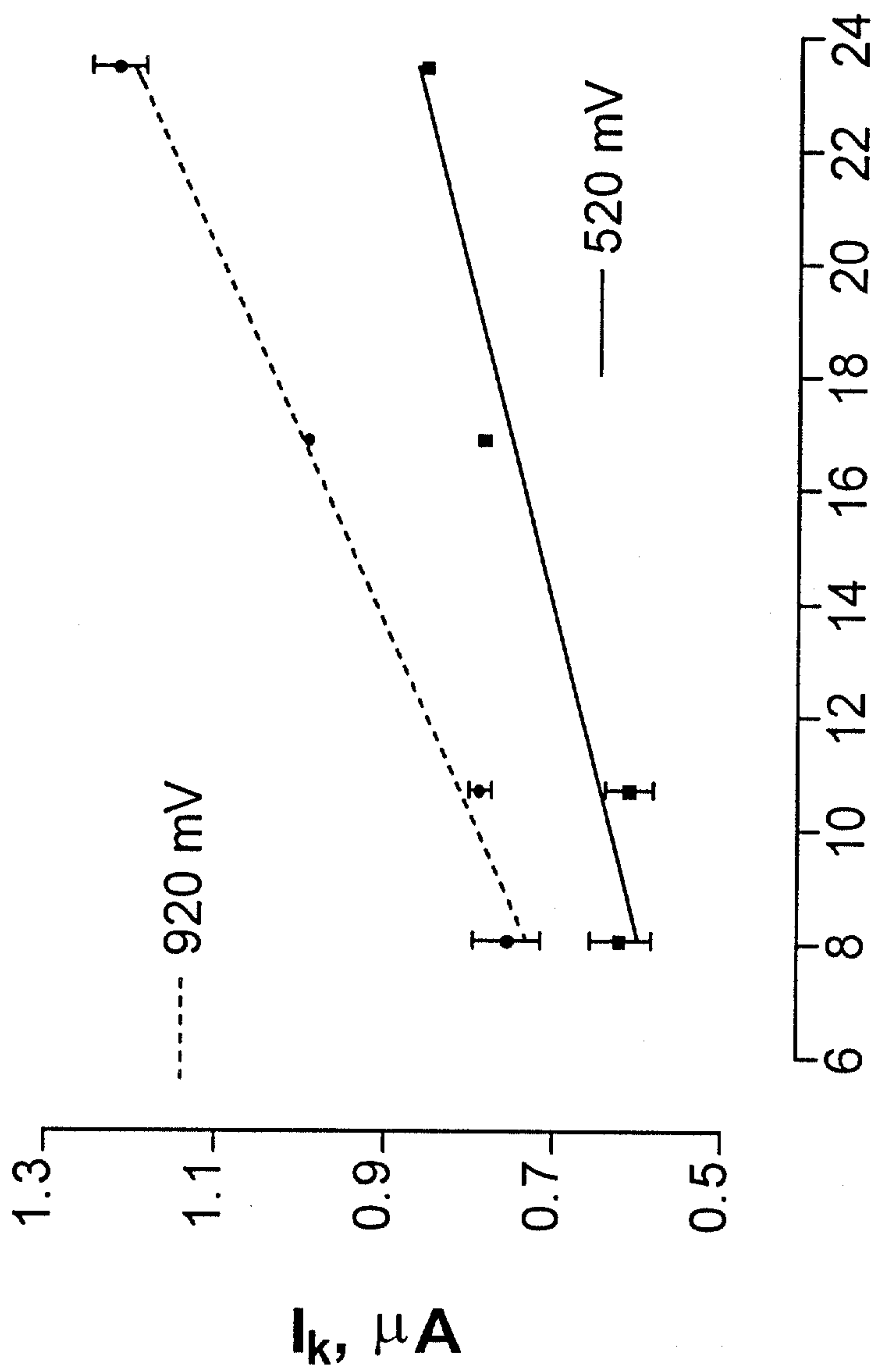
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FEF-5



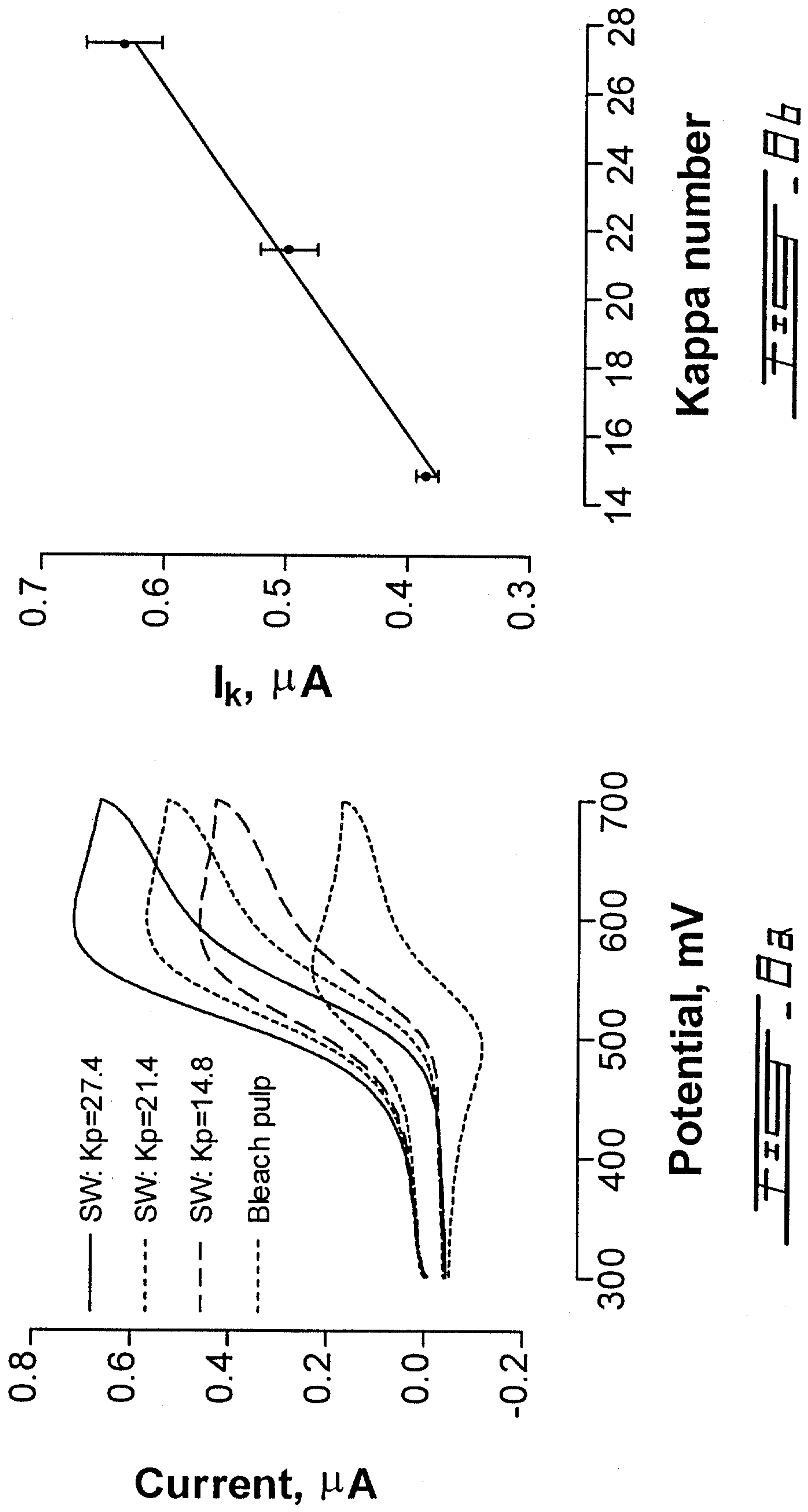
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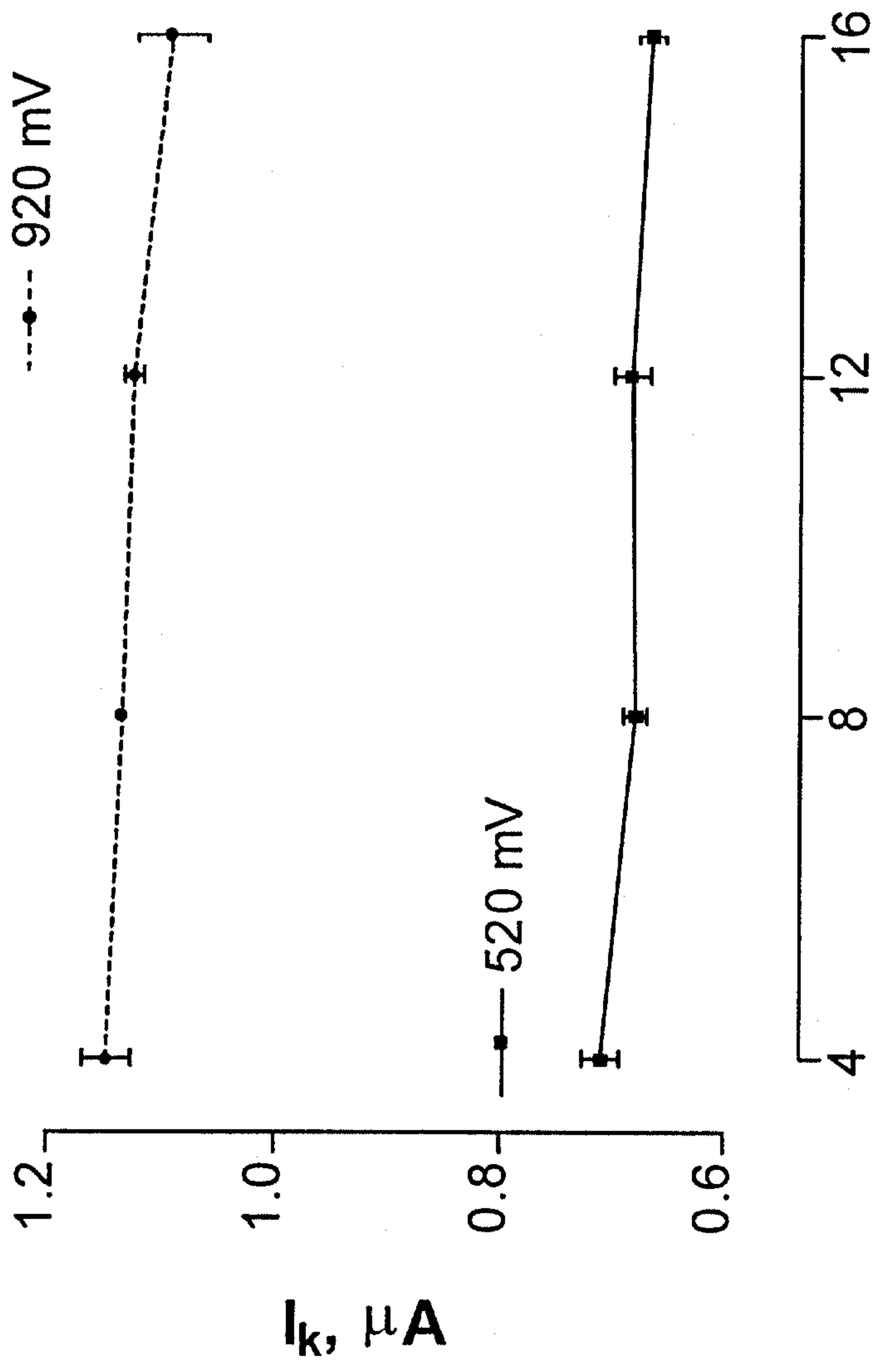
TABLE 1



Kappa number

7





Pulp sample size, mg

FIG. 9

