

1 **Potentiometric Determination of Coextraction Constants**  
2 **of Potassium Salts in Ion-Selective Electrodes Utilizing a**  
3 **Nitrobenzene Liquid Membrane Phase**

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1 **Abstract**

2 A theoretical treatment of potentiometric data is applied to calculate coextraction  
3 constants ( $K_{IA}$ ) for three potassium salts from water into a liquid nitrobenzene phase.  
4 The experiment involves treating nitrobenzene as a membrane and contacting it with  
5 two aqueous solutions of different ion activities. In the presence of either a cation or  
6 anion exchanger, the ratio of activities of ions in the two aqueous phases gives rise to  
7 a potential difference across the membrane that depends upon the nature and charge  
8 of the counter ion of the ion-exchanger in excess. Here, the cation exchanger was  
9 chosen to be potassium tetrakis(4-chlorophenyl)borate (KTPCIPB) and the anion  
10 exchanger was tetradodecylammonium chloride (TDDACl). TDDACl was  
11 incrementally added to the nitrobenzene phase containing a fixed concentration of  
12 KTPCIPB, and the corresponding emf was recorded as a function of concentration of  
13 TDDACl. The membrane changes from one with cation exchanger properties (excess  
14 KTPCIPB) to one with anion exchanger properties (excess TDDACl). The potential  
15 difference and shape of the titration curve can be predicted by theory based on the  
16 phase boundary potential model.  $\text{Log}(K_{IA})$  values calculated for KCl,  $\text{KNO}_3$  and  
17  $\text{KClO}_4$  in nitrobenzene were found as:  $-10.53 (\pm 0.09)$ ,  $-8.16 (\pm 0.05)$  and  $-5.63 (\pm$   
18  $0.03)$  respectively, in accordance with the Hofmeister series of lipophilicity, and  
19 similar to those observed in PVC membranes containing other plasticizers. The  
20 method presented here offers the advantage over other methods to calculate  $K_{IA}$ , in  
21 that it is relatively experimentally simple without compromising the accuracy of the  
22 calculated coextraction constants. The ability to titrate directly into the liquid  
23 membrane phase affords a higher precision compared to the preparation of a series of  
24 PVC/plasticizer membranes with different compositions.

25

26 **Keywords**

27 Potentiometry, nitrobenzene, ITIES, phase boundary potential, coextraction constant,  
28 chloride, nitrate, perchlorate.

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## 1 **1. Introduction**

2 Ion-selective electrodes (ISEs) are common tools used in many types of chemical  
3 analyses [1, 2]. They are typically comprised of a polymeric membrane matrix (e.g.  
4 PVC (poly(vinyl chloride))/plasticizer) containing both an ion-exchanger and  
5 ionophore in appropriate quantities. The membrane is contacted on one side with an  
6 aqueous inner solution (usually containing a Ag/AgCl wire as the working electrode)  
7 and on the other side with the sample solution. ISEs employing these types of  
8 membranes are robust, reliable and sensitive, however their preparation requires  
9 careful precision in the weighing of each component in the polymer matrix, and a  
10 relatively long time to condition the electrodes (usually ~12 hours). In this  
11 fundamental work, the solid PVC/plasticizer membrane has been replaced with a  
12 liquid nitrobenzene phase, offering the advantage of easy membrane preparation and  
13 no need for a conditioning step. The transfer of ions across the phase boundaries in  
14 this type of system can be monitored by potentiometry at the ITIES [3-5] (interface  
15 between two immiscible electrolyte solutions), and the phase-boundary potential  
16 model can be used to predict the measured emf.

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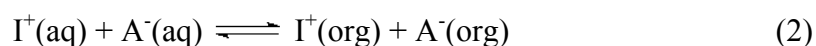
18 We recently introduced a potentiometric method at the ITIES to monitor the ion-  
19 exchange properties of a nitrobenzene organic phase containing either excess cation-  
20 exchanger or excess anion-exchanger, in contact with two aqueous phases containing  
21 potassium chloride with different ion activity [6]. The two salts used as the cation and  
22 anion exchanger in the organic phase were KTpCIPB (potassium tetrakis(4-  
23 chlorophenyl)borate) and TDDACl (tetradodecylammonium chloride), respectively. It  
24 was predicted by theory that the potential jump from excess cation exchanger to  
25 excess anion exchanger, is related to the ratios of the activities of electrolyte in the  
26 aqueous phases, given by the Nernst equation:

$$27 \quad E = \frac{RT}{z_1 F} \ln \frac{a_1(aq_1)}{a_1(aq_2)} \quad (1)$$

28 where  $E$ =membrane potential,  $z_1$ =charge on the uncomplexed ion (+1 or -1) and  
29  $a_1$ =activity of the uncomplexed ion I, in the two indicated aqueous phases.  $R$ ,  $T$  and  $F$   
30 are the universal gas constant, the absolute temperature and the Faraday constant,  
31 respectively. This equation allows the calculation of the overall  $\Delta E$  for the titration,  
32 but does not give any information on other parameters, such as the magnitude of the  
33 coextraction constant of the salt present the aqueous phase. As a result, in this work,

1 we have extended the above method by fitting the experimental titration curves of  
2 three potassium salts (present at fixed concentrations in the aqueous phase) to theory,  
3 allowing for the direct estimation of coextraction constants (see Theory section).

4  
5 It is well established that the upper detection limit of both potentiometric and optical  
6 sensors is affected by coextraction of the analyte ion and its counter-ion into the  
7 organic phase, according to the following reaction [7]:



9 Where  $\text{I}^+$  is the electrolyte cation and  $\text{A}^-$  is the electrolyte anion. The coextraction  
10 constant ( $K_{IA}$ ) is given by the relative lipophilicity of the anion and cation and the  
11 complex formation constant of the ionophore. It is useful to have knowledge of the  
12 magnitude of coextraction constants in various membrane matrices, in order to select  
13 the correct electrolyte salt to give the optimum sensor response range.

14  
15 There have been several techniques employed to date in order to calculate  
16 coextraction constants. For example, Qin and Bakker [8] devised a sandwich  
17 membrane technique, with one half of the membrane containing a lipophilic cation  
18 exchanger and the other half containing an anion exchanger. This was used to  
19 elucidate coextraction constants for many salts from water into PVC/NPOE (*o*-  
20 nitrophenyl octyl ether). The magnitudes of the log of coextraction constants varied  
21 between -6.7 and -15.8, and were found to depend on the relative lipophilicities of the  
22 ions, according to the Hofmeister sequence [9]. The drawback to this method is that a  
23 large number of membranes with appropriate concentrations of ion-exchanger sites  
24 were required, which can be inconvenient and quite time-consuming. Two  
25 voltammetric methods have also been proposed to calculate coextraction constants.  
26 Jadhav and Bakker [10] determined coextraction constants of ions from an ionophore-  
27 free plasticized PVC membrane and estimated a value of -9.6 for  $\text{Log}(K_{IA})$  of NaCl  
28 into a PVC/DOS (bis(2-ethylhexyl)sebacate) membrane. This method suffers from the  
29 drawback that the potential asymmetries of the cell need to be corrected so that the  
30 coextraction constant can be calculated more accurately. Lo and Choi [11] devised a  
31 symmetrical voltammetric cell in order to overcome the problem of the potential  
32 asymmetries of such a cell. They calculated coextraction constants for various sodium  
33 salts with different anions and various chloride salts with different cations. The  
34 magnitudes of  $\text{Log}(K_{IA})$  varied between -4.8 and -11.9 in PVC/NPOE membranes,

1 and they were also found to follow the Hofmeister sequence. However, this method,  
2 although rapid and experimentally simple, suffers from a much larger error due to the  
3 way the voltammetric curve is extrapolated. As a result, there was a rather large  
4 discrepancy (2-4 orders of magnitude) between coextraction constants using the  
5 symmetrical cell compared to those reported by Qin and Bakker [8], despite using the  
6 same membrane material. The work presented in this article describes a new and  
7 experimentally simple method to calculate coextraction constants for various salts,  
8 based on potentiometry in a liquid membrane phase (nitrobenzene) containing a fixed  
9 concentration of cation exchanger (KTPCIPB) and an incrementally increasing  
10 concentration of anion exchanger (TDDACl). The use of a liquid membrane allows  
11 the ability to titrate directly into the membrane and gives a detailed picture over the  
12 whole concentration range, which can be extremely difficult and time consuming to  
13 obtain in common PVC/plasticizer membranes.

14

## 15 **2. Experimental**

### 16 *2.1 Chemicals*

17 Potassium chloride (KCl, Fluka  $\geq 99.5\%$ ), potassium nitrate ( $\text{KNO}_3$ , Fluka  $\geq 99\%$ ),  
18 potassium perchlorate ( $\text{KClO}_4$ , Fluka,  $>99.5\%$ ), potassium tetrakis(4-  
19 chlorophenyl)borate (KTPCIPB, Fluka  $\geq 98\%$ ) and tetradodecylammonium chloride  
20 (TDDACl, Fluka  $\geq 97\%$ ) were used as received. Nitrobenzene (NB, Sigma-Aldrich  
21 99%) was first washed several times in a solution of 0.1 M NaOH (NaOH, APS  
22 Finechem  $>97\%$ ) in water to remove coloured impurities initially present in the NB  
23 (e.g. nitrophenol), then with water to remove any residual NaOH. A solution of 0.1 M  
24 sodium bicarbonate ( $\text{NaHCO}_3$ , BDH  $\geq 99.7\%$ ) was adjusted to pH 7 using 1M HCl,  
25 and was used as the aqueous buffer.

26

27

### 28 *2.2 Potentiometry*

29 A 16-channel mV-meter (Lawson Labs Inc., Malvern, PA) was used to conduct  
30 potentiometric experiments in a stirred solution at room temperature ( $22 \pm 1$  °C). The  
31 “reference” electrode was connected to a Ag/AgCl wire, which was immersed in an  
32 aqueous solution (*ca.* 3 mL of either 1 M KCl, 1 M  $\text{KNO}_3$  or 0.1 M  $\text{KClO}_4$ ), inside a  
33 glass pipette. The “working” electrode was connected to an identical Ag/AgCl wire,

1 immersed in 3 mL of the same electrolyte (either  $10^{-2}$  M KCl,  $10^{-2}$  M KNO<sub>3</sub> or  $10^{-3}$  M  
2 KClO<sub>4</sub>) in a glass pipette. The aqueous solutions not containing KCl incorporated a  
3 background electrolyte concentration of  $10^{-3}$  M KCl in order to maintain a stable  
4 potential at the Ag/AgCl wire. The tips of the glass pipettes were modified with  
5 Celgard 2500 (a polypropylene porous membrane- acting here only as a diaphragm) to  
6 prevent leaking/mixing of the aqueous and organic phases, and to allow transfer of  
7 ions through the phase boundary. Both electrodes were immersed directly into the  
8 lower organic phase of a two-phase system containing  $10^{-4}$  M KTpClPB in NB (10  
9 mL) and an aqueous bicarbonate buffer (~2 mL, pH 7). TDDACl ( $10^{-2}$  M) was titrated  
10 into the organic phase in small increments, and the potential was monitored as a  
11 function of the number of moles of TDDACl. All experiments were performed in a  
12 fume cupboard. The cell can be written in shorthand notation as: Ag(s)/AgCl(s)/1 M  
13 KCl(aq)/celgard membrane/ $10^{-4}$  M KTpClPB + X mM TDDACl in nitrobenzene  
14 (org)/celgard membrane/ $10^{-2}$ M KCl(aq)/AgCl(s)/Ag(s). Figure 1 shows a detailed  
15 schematic of the electrochemical cell.

16

### 17 **3. Theory**

18 Based on our recent work [6], it is possible to predict the potential jump,  $\Delta E$ , resulting  
19 from the titration of excess anion exchanger into a membrane phase containing a  
20 known concentration of cation exchanger (see equation (1)). The experiment involves  
21 treating the polar organic solvent, nitrobenzene, as a membrane phase, and contacting  
22 it with two aqueous phases of different ion activity. The mismatch in electrolyte  
23 activity gives rise to a membrane potential difference across the cell. Here, the theory  
24 has been extended to allow for the calculation of coextraction constants of electrolyte  
25 from water to nitrobenzene. The curve is generated in two parts; the first half is the  
26 result of the cation-exchanger response of the membrane, until the membrane  
27 potential is zero, and the second half is the anion-exchanger response. The theory  
28 presented here describes the first half of the curve (cation exchanger response), but  
29 the same equations are also used for the anion exchanger response. Equations for ion-  
30 pairing were not included, since it is assumed that ion-pairing does not play a  
31 significant role in polar membranes [12].

32

1 We consider the coextraction constant,  $K_{IA}$ , for the partitioning of the cation,  $I^+$ , and  
 2 anion,  $A^-$ , from the aqueous phase into the organic phase according to the following  
 3 equation [7]:

$$4 \quad K_{IA} = \frac{[I^+]_{org} [A^-]_{org}}{a_{I^+} a_{A^-}} \quad (3)$$

5 where  $[I^+]_{org}$  and  $[A^-]_{org}$  are the concentrations of  $I^+$  and  $A^-$  in the organic phase, and  
 6  $a_{I^+}$  and  $a_{A^-}$  are the activities of  $I^+$  and  $A^-$  in the aqueous phase. As  $R^+A^-$  is titrated into  
 7 the organic phase, the charge balance equation is formulated as:

$$8 \quad ([I^+]_{org} + [A^-]_{org})V_{org} = n_{R^-} - n_{R^+} \quad (4)$$

9 where  $n_{R^-}$  and  $n_{R^+}$  are the number of moles of cation exchanger and anion exchanger,  
 10 respectively, and  $V_{org}$  is the volume of the organic phase.

11 If we combine equations (3) and (4), while eliminating  $[A^-]_{org}$ , the following  
 12 expression is obtained in terms of  $[I^+]_{org}$ :

$$13 \quad K_{IA} [I^+]_{org}^2 + \frac{K_{IA} (-n_{R^-} + n_{R^+})}{V_{org}} = a_{I^+} a_{A^-} K_{IA}^2 \quad (5)$$

14 While taking into account the different activities of ions in the two different  
 15 contacting aqueous phases, the membrane potential is given by the difference between  
 16 the potentials at the two phase boundaries [13]:

$$17 \quad E_M = \frac{RT}{F} \log \frac{a_{I^+}'' [I^+]'_{org}}{a_{I^+}' [I^+]''_{org}} \quad (6)$$

18 Where the prime and double prime symbols denote activities/concentrations at the  
 19 outer and inner phase boundaries of the liquid membrane phase, respectively. The  
 20 potential can be calculated at all concentrations of added anion exchanger by solving  
 21 equation (5) for  $[I^+]_{org}$  for each phase boundary and inserting the results into equation  
 22 (6). While all other parameters are known (defined at the start of the experiment), the  
 23 value of coextraction constant is varied until the best fit to experimental data is  
 24 obtained.

25

26 In the examples where anions other than chloride are employed, a background of  $10^{-3}$   
 27 M KCl was added to maintain a constant potential at the Ag/AgCl elements. As a  
 28 result, an additional parameter was added to equation (6) to account for the extra  
 29 chloride concentration:

1 
$$emf = \frac{RT}{F} \log \frac{a_{Cl^-}'}{a_{Cl^-}''} \quad (7)$$

2 where  $a_{Cl^-}$  is the activity of chloride ions in the first (') and second (') contacting  
3 aqueous phases. A similar treatment was applied to describe the second half of the  
4 curve (anion exchanger response), which was combined with the cation exchanger  
5 response to give a theoretical curve over the whole titration range. The value for the  
6 coextraction constant was varied until the best fit to the experimental data was  
7 obtained.

8

#### 9 **4. Results and Discussion**

10 Since it has previously been reported [8] that the upper detection limit of ISEs is  
11 determined partly by the coextraction of electrolyte salts into the membrane phase, it  
12 seems important to describe a method to calculate coextraction constants from water  
13 to nitrobenzene. The method employed here is used to calculate coextraction  
14 constants for three potassium salts from water to nitrobenzene. The experimental set-  
15 up is shown in Figure 1, and uses simple equipment that is available in any standard  
16 laboratory. As described in the theory section, the phase boundary potential model can  
17 be used to calculate coextraction constants by fitting standard equations to the data  
18 obtained from potentiometric experiments.

19

20 Here, an anion exchanger is titrated into a membrane phase containing only a cation  
21 exchanger at a fixed concentration. The salts used as the cation and anion exchanger  
22 were chosen to be KTpCIPB and TDDACl, respectively, for reasons described in our  
23 recent publication [6]. The organic phase is in contact with two aqueous phases,  
24 separated by a Celgard porous membrane, to prevent the mixing of the phases whilst  
25 allowing ion-transfer across the phase boundaries. Based on theory, the shape on the  
26 titration curve is dictated by the coextraction constant of the electrolyte used in the  
27 aqueous phases. For a more lipophilic salt, the potential jump ( $\Delta E$ ) is predicted to be  
28 smaller, and the slope of the titration curve is expected to be more flat. Figure 2 shows  
29 the experimental data points (dots) for the titration of TDDACl into an organic phase  
30 containing  $10^{-4}$  M KTpCIPB. The three figures correspond to the titration curves  
31 obtained when the nature of the electrolyte in the two contacting aqueous phases is  
32 changed from (A) KCl, (B) KNO<sub>3</sub> and (C) KClO<sub>4</sub> (in order of increasing



1 lipophilicity). The concentration of electrolyte in one aqueous phase was chosen to be  
2 as high as possible, with the second aqueous phase possessing two orders of  
3 magnitude smaller concentration. For KCl and KNO<sub>3</sub>, the concentrations employed  
4 were 1 M and 10<sup>-2</sup> M, and due to the limited solubility, KClO<sub>4</sub> was chosen to be 0.1 M  
5 and 10<sup>-3</sup> M. In the case of KNO<sub>3</sub> and KClO<sub>4</sub>, a background electrolyte concentration  
6 of 10<sup>-3</sup> M KCl was also added to maintain a constant potential at the Ag/AgCl wires  
7 (this was taken into account in the theory).

8  
9 Also shown in Figure 2 is the best theoretical fit (solid line) to the experimental data  
10 points. As can be seen, an excellent agreement is observed between experiment and  
11 theory. The potential jump ( $\Delta E$ ) from theory for all three salts is given in Table 1.  $\Delta E$   
12 decreases in the order KCl > KNO<sub>3</sub> > KClO<sub>4</sub>, according to the Hofmeister series. The  
13 calculated coextraction constants ( $K_{IA}$ ) for the best-fit curves shown in Figure 2 are  
14 given in Table 1. The magnitudes of  $K_{IA}$  and associated errors were calculated using  
15 non-linear least squares fitting methods providing the best fit to experimental data. As  
16 can be seen, the differences in Log( $K_{IA}$ ) relative to KClO<sub>4</sub> is -2.5 and -4.9 for KNO<sub>3</sub>  
17 and KCl, respectively. This is not unexpected, since similar behaviour has been  
18 observed in conventional membranes (-3.1 and -5.2 in PVC/NPOE) [8]. These  
19 coextraction constants suggest that nitrobenzene is a hydrophobic solvent where small  
20 electrolytes are difficult to extract without mediation by an ionophore. Based on the  
21 relative magnitudes presented in the table, it is more difficult to extract chloride into a  
22 nitrobenzene membrane (containing ion-exchanger) than both nitrate and perchlorate.  
23 These results suggest that nitrobenzene membranes behave in a similar way to  
24 traditional PVC/NPOE membranes. By replacing a traditional membrane with a liquid  
25 phase, however, allows the ability to change the concentration of species in the  
26 membrane phase quickly and easily so that important fundamental parameters, such as  
27 the coextraction constant, can be obtained.

## 28 29 **5. Conclusions**

30 The potentiometric method and corresponding theoretical treatment presented here  
31 has been used to calculate coextraction constants for three potassium salts in an  
32 organic nitrobenzene liquid phase. The coextraction constants were found to follow  
33 the order of the Hofmeister sequence (ClO<sub>4</sub><sup>-</sup> > NO<sub>3</sub><sup>-</sup> > Cl<sup>-</sup>) based on the relative  
34 lipophilicities of the ions [9]. The relative magnitudes of the coextraction constants

1 are similar to those obtained for the same salts in conventional PVC/plasticizer  
2 membranes. The method used in this work has advantages over both the sandwich  
3 membrane method [8] and the voltammetric extrapolation method [11] previously  
4 reported, since it is relatively experimentally simple, an excellent agreement of  
5 experiment with theory is observed. In addition, using potentiometry eliminates any  
6 additional effects (e.g. Faradaic currents) that can often be observed with  
7 voltammetry.

8

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12

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16  
17

1 **Table 1**

2 Coextraction constants ( $K_{IA}$ ) of three potassium salts from water into a nitrobenzene  
3 liquid membrane, calculated by non-linear least squares fitting methods providing the  
4 best agreement with experimental data curves shown in Figure 2.

5

Potassium Salt	$\Delta E$ (theoretical) / mV	Log ( $K_{IA}$ )
KCl	214 ( $\pm$ 4)	-10.53 ( $\pm$ 0.09)
KNO <sub>3</sub>	192 ( $\pm$ 3)	-8.16 ( $\pm$ 0.05)
KClO <sub>4</sub>	173 ( $\pm$ 3)	-5.63 ( $\pm$ 0.03)

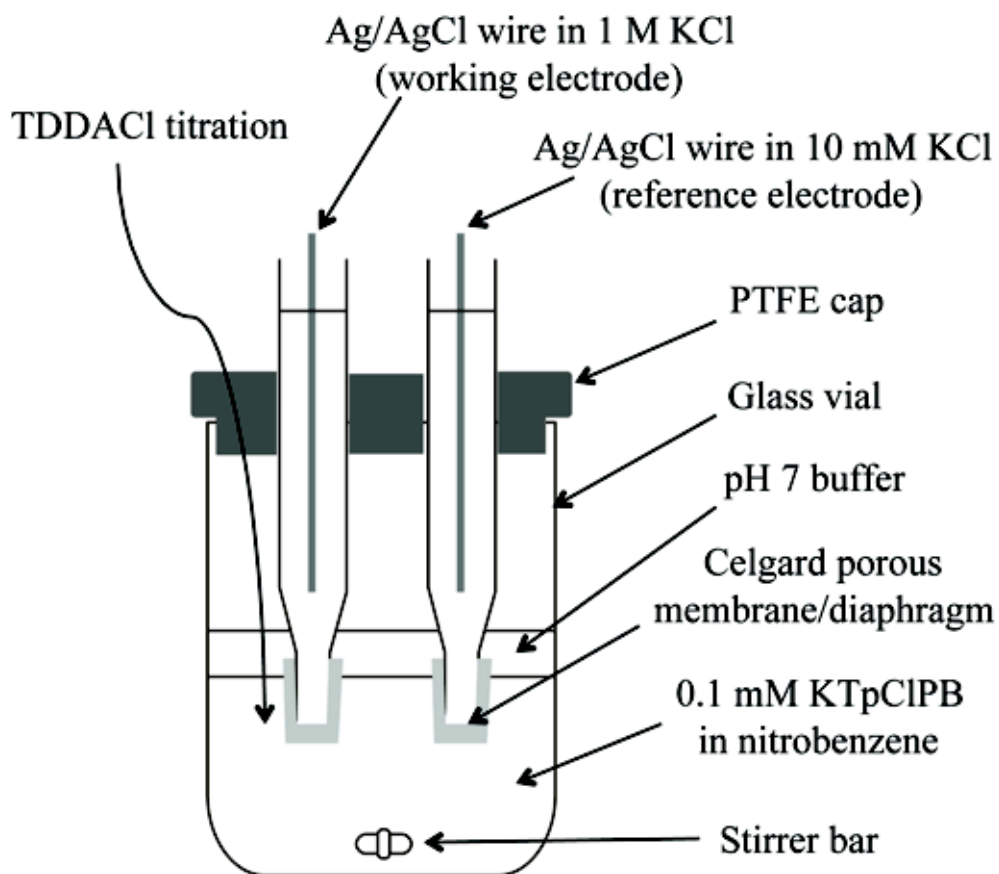
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1 **Figures**

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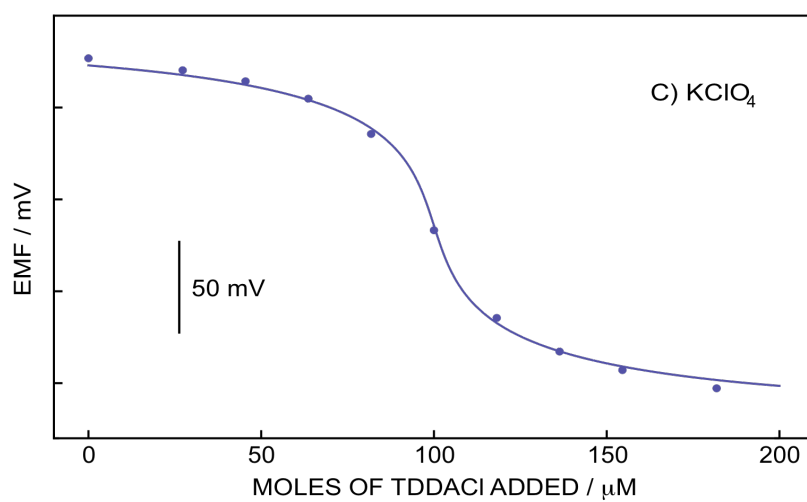
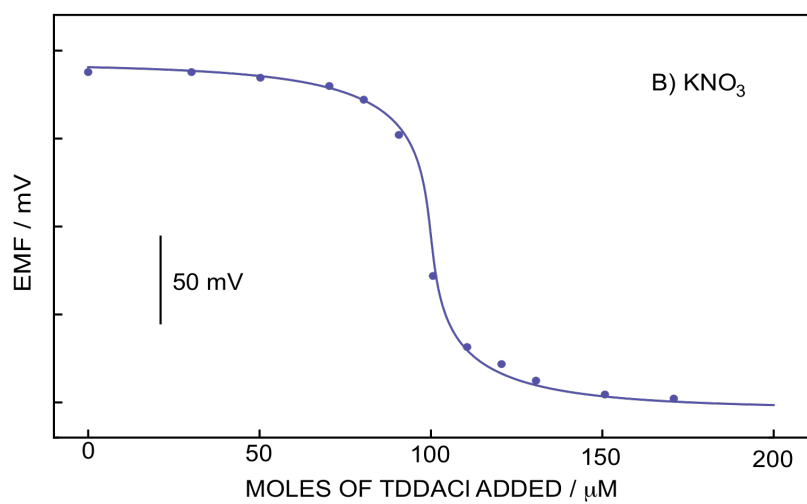
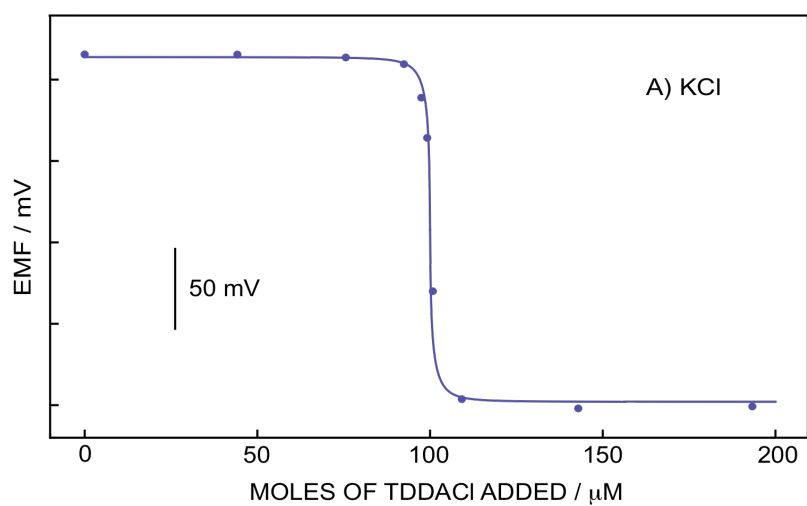
3 Figure 1.

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1 Figure 2.



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3

1 **Figure Captions**

2 Figure 1.

3 Schematic of the electrochemical cell used for potentiometry experiments, utilizing  
4 nitrobenzene as the liquid organic “membrane” phase.

5

6 Figure 2.

7 Experimental data points (dots) and theoretical curves for TDDACl titration into  $10^{-4}$   
8 M KTpClPB in a nitrobenzene phase contacted with pH 7 bicarbonate buffer.  
9 Electrolyte compositions used in the two aqueous phases are: (A) 1 M and  $10^{-2}$  M  
10 KCl, (B) 1M and  $10^{-2}$  M  $\text{KNO}_3$  and (C)  $10^{-1}$  M and  $10^{-3}$  M  $\text{KClO}_4$ .  $10^{-3}$  M KCl was  
11 employed as a background electrolyte in solutions not containing chloride.