# MEMBRANE ELECTRODES OF HERBICIDAL AND PHARMACEUTICAL INTEREST[a]

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Researches on PVC matrix membrane electrodes based on crown ethers are reviewed for diquat, paraquat and guanidinium. The crown ethers for diquat and paraquat consist of dibenzo-30-crown-10 (DB30C10), bis-metaphenylene-32-crown-10 (BMP32C10), bis-metaphenylene-38-crown-12 (BMP38C12), bis-paraphenylene-34-crown-10 (BPP34C10), bis-paraphenylene-37-crown-11 (BPP37C11), and dinaphthalene-36-crown-10 (DN36C10). The data are discussed in terms of the quality of potentiometric response related to conformational phenomena of the crown ethers in their complexation with the two dications and with the related 4,4'-dipyridinium. The best electrodes for diquat and paraquat are based on DB30C10 and DQT.2TPB with 2-nitrophenyl phenyl ether, while good paraquat electrodes are based on PQT.2TPB with either 2-nitrophenyl phenyl ether or 2-nitrophenyl octyl ether.

The remaining crown ethers give good 4,4'-dipyridinium electrodes with dibutyl phthalate as solvent mediator. The anticipated good paraquat electrode did not materialize for BPP34C10 as sensor, probably because of inadequate stability of the complex with paraquat because of weaker electrostatic effects than are available for 4,4'-dipyridinium.

Guanidinium electrodes are discussed in terms of the best being based on dibenzo-27-crown-9 in PVC membranes plasticized with dibutyl phthalate. The presence of tetraphenylborate leads to less sensitive and more sluggish electrode response.

Also reviewed is work on prospects for other anion excluders in ISE membranes instead of tetraphenylborate. The best prospect is for tetrakis-4-chlorophenylborate being better than tetraphenylborate, while picrate is not sufficiently lipophilic. Five

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other systems are totally unsuitable. The analogy between ISE function and ion-pair extraction into an organic phase is also discussed for these systems with some correlation being evident.

1. INTRODUCTION

2. ISEs FOR DIQUAT AND PARAQUAT BASED ON DIBENZO-30-CROWN-10
   2.1 Diquat Electrodes
   2.2 Paraquat Electrodes

3. DICATION (DIQUAT, PARAQUAT AND 4,4'-DIPYRIDINIUM) SENSING WITH A RANGE OF CROWN ETHERS
   3.1 Diquat and Paraquat Electrodes
   3.2 4,4'-Dipyridinium Electrodes

4. ELECTRODES FOR GUANIDINIUM $[(H_2N)_3C]^+$

5. ELECTRODES FOR DICATIONS BASED ON ION-PAIRING AGENTS
   5.1 Interaction with Ion-pairing Agents
   5.2 ISE Function and Ion-pair Extraction into Organic Phase

6. CONCLUSION

7. REFERENCES

KEYWORDS: Crown ether ion sensors, ion-selective electrodes, diquat, paraquat, 4,4'-dipyridinium, guanidinium, dication electrodes, ion-pair extraction.

## 1. INTRODUCTION

Ion-selective electrodes (ISEs) based on neutral carrier ligands are now well established[1] following the use of valinomycin and other naturally occurring antibiotic compounds, e.g., macrotetrolides, for potassium and



ammonium ISEs.[2,3] Synthetic neutral carriers, such as the cyclic polyethers (crown ethers)[4] have since been produced. Of these, dodecylmethyl-14-crown-4 has yielded an interesting lithium ISE,[5] and bis(crown ether) derivatives of 15-crown-5 and 18-crown-6 have yielded potassium and caesium ISEs.[6]

The selection of suitable neutral carriers for ion-sensing can be helped by structural studies on interactions between carriers and ions. In this respect, Stoddart and co-workers have shown (for a list of the relevant references, see Reference 7 of this paper) interesting features on the interactions between macrocyclic polyethers and molecules and cations. The bonding was classified under three main headings:

(i) coordination via [N-H···O] hydrogen bands as in complexation between polyether and primary alkylammonium ions[8,9]
(ii) coordination through [C-H···O] linkages to the diquat (DWT) dication,[10] etc., and
(iii) metal ion coordination to oxygen atoms of the crown ether compound.

There is considerable incentive for using the structural information obtained by Stoddart and co-workers, especially in respect of that directed to diquat (DQT) and paraquat (PQT) dications. The use of these as contact herbicides lends priority to methods for their determination, and the structural studies relating to their complexation with DB30C10 suggested the use of the crown ether as an ISE sensor.[7] The structural data were based on X-ray crystallographic structure determination of the complex between the $DQT^{2+}$ dication and DB30C10 where the gross host-guest structural features are of the above category (ii) type of hydrogen bonding and charge transfer to give stable and ordered 1:1 solution

complexes between DB30C10 and DQT bis(hexafluorophosphate).[10]

The maximum stability for DB3nCn complexes with DQT occurs when n = 10[11-14] (Table 1) while the X-ray structure shows the plane of the DQT molecule to be enclosed in a U-shaped cavity formed by DB30C10[10,11] as confirmed by nmr studies for the complex in solution.[12,13] The complexation involves three DB30C10(host)-DQT(guest) interactions:-

(i) DB30C10 catechol-oxygen electrostatic interaction with the positively charged nitrogen atoms in DQT. For this, the crown ether catechol 0-0 separation (2.6Å) and N-N separation in DQT (2.8Å) are similar so that the former are nearly directly above and below the latter in the $[DQT.DB30C10]^{2+}$ complex.

(ii) DB30C10 benzene ring π-electron charge transfer to the electron deficient $DQT^{+}$.

(iii) Hydrogen bonding between $H^{6}$ and $H^{6'}$ (Fig.1) with oxygen atoms in the DB30C10 framework, and as previously mentioned above.

Table 1. Stability constants ($K_a$) and free energies of formation ($\Delta G_f$) of [DQT.DB3nCrown-n] complexes in acetone[a]. (From Ref.15)

| Crown ether | $K_a(M^{-1})$ | $\Delta G_f/kJ\ mol^{-1}$ |
|---|---|---|
| DB27C9 | $4.1 \times 10^{2}$ | 15.0 |
| DB30C10 | $1.8 \times 10^{4}$ | 24.3 |
| DB33C11 | $1.1 \times 10^{4}$ | 23.1 |
| DB36C12 | $2.0 \times 10^{3}$ | 18.9 |
| $DB30C10(-OCH_2)_2Ph$ | - | 31.0 |

a Data from Refs. 11, 12 and 14



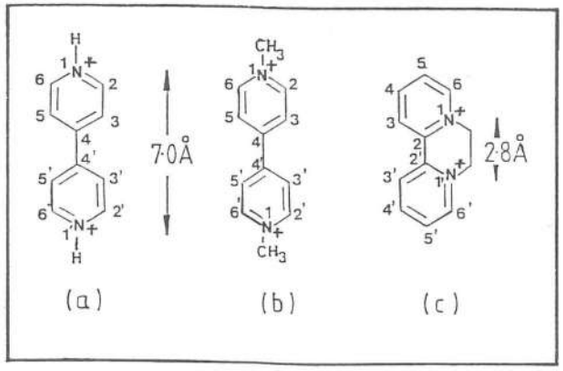


Fig.1 Chemical structures of (a) 4,4'-dipyridinium, (b) paraquat, and (c) diquat, showing some dimensions and more acid hydrogen atoms (from Ref.15)

The guanidinium cations, $[(H_2N)_3C]^{+}$, can complex with crown ethers of between 18 and 33 ring atoms.[16-18] Crown ethers of 27 members are the most selective to guanidinium, and the possibility of guanidinium electrodes is of interest in view of the importance of guanidine in the biological and medical fields.

This paper reviews studies on ISEs for DQT, PQT and guanidinium. The dication electrodes are also compared with systems for their 4,4'-dipyridinium analogue, when attention is paid to the rôle of anion excluders in ISE membranes and of the ISE function of these on their own.

## 2. ISEs FOR DIQUAT AND PARAQUAT BASED ON DIBENZO-30-CROWN-10

PVC matrix membrane ISE types were assembled according to established practice[19] with membrane composition[7] according to Table 2. The emfs of the various ISEs were measured with respect to a saturated calomel electrode.[7]

The three types of electrodes were assessed for different solvent mediators[7] and the main response features are summarized in Table 3 of which the parameters relate to the linear regression line

$$\Delta E(mV) = S \log a + C \qquad (1)$$

where S, a and C, respectively, are the electrode calibration slope (mV/log a), the activity of the sensed ion (mol $dm^{-3}$), represented by M and the response intercept (mV).

Table 2 Composition of PVC matrix membrane types used for electrode construction (from Ref.7)

| Membrane | Membrane Composition, % mass ratio | | | |
|---|---|---|---|---|
| | Solvent mediator | PVC | DB30C10 | DQT.2TPB or PQT.2TPB |
| 1 | 67.0 | 31.6 | 1.4 | - |
| 2 | 62.3 | 29.4 | 1.3 | 7.0 |
| 3 | 63.0 | 30.0 | - | 7.0 |

Most of the electrodes gave a dynamic 95% steady-state response within 30 s, while electrodes transferred from test solutions to water quickly attained "background" potential.[7] The notable exception was the DOPP-based electrodes with a steady-state response of about 5 min at sample activities of $<5 \times 10^{-5}$M. All the ISEs had a useful pH range[7] of about 1.2 to 8.5. Generally, between pH 9.0 and 9.5 (and at higher pHs) there was a sudden change in colour of the DQT solution from light yellow to red.[7] This was followed by an increase in electrode response with time, but normal response was restored on immersion in solutions of pH between 4.5 and 6.0.



Table 3 Response features of ISEs for DQT. Standard deviations in parentheses are for n = 5-7, spread over 7 d. (from Ref.7)

| Solvent mediator[a] | Type 1 | | | | Type 2 | | | | Type 3 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | S/mV | C/mV | $a_{min}$ /$10^{-6}$M | r | S/mV | C/mV | $a_{min}$ /$10^{-6}$M | r | S/mV | C/mV | $a_{min}$ /$10^{-6}$M | r |
| DBP | 35.6 (3.3) | 179 (15.7) | 9.7 (2.2) | 0.991 | 25.2 (0.35) | 135 (3.1) | 4.2 (0.4) | 0.998 | 34.1 (0.6) | 186 (5.3) | 3.5 (0.8) | 0.998 |
| DNP | b | b | b | b | 17.5 (1.1) | 8.1 (1.6) | 24 (11) | 0.89 | 27.3 (1.2) | 114 (10) | 430 (360) | 0.987 |
| DOPP | 47.0[c] | 233 | 11 | 0.998 | 21.8 (0.2) | 105 (2.0) | 16 (2) | 0.997 | 27.0 (2.2) | 149 (3.4) | 3.3 (2) | 0.997 |
| NPOE | 32.6 (2.1) | 151 (18.7) | 31 (24) | 0.989 | 28.8 (0.6) | 170 (6.4) | 1.5 (1.1) | 0.999 | 31.2 (1.9) | 160 (27) | 18 (20) | 0.998 |
| NPPE | b | b | b | b | 29.8 (1.4) | 169 (11) | 1.4 (0.4) | 0.999 | 26.7 (0.9) | 153 (5.3) | 1.8 (0.4) | 0.999 |

a DBP = dibutyl phthalate, DNP = dinonyl phthalate, DOPP = dioctylphenyl phosphonate, NPOE = o-nitrophenyl octyl ether, and NPPE = o-nitrophenyl phenyl ether

b Functional electrodes not obtained

c Electrode slope unstable

2.1 Diquat Electrodes

Type 1 electrodes tended to be more unstable.[7] Selectivity for DQT over other cations is greatly improved after addition of DQT.2TPB to the membrane to yield type 2 electrodes. Electrodes based entirely on DQT.2TPB (type 3) also gave very good characteristics[7] with appropriate solvent mediators, and further studies on these and similar systems are discussed below. However, for both type 2 and type 3 electrodes, the best solvent mediators[7] are either 2-nitrophenyl phenyl ether (NPPE) or 2-nitrophenyl octyl ether (NPOE).

Selectivity coefficient data ($k^{pot}_{DQT,B}$) were determined[7] for B = Li, Na, K, Mg, Ca, Ba, ammonium, diethylammonium, anilinium, and guanidinium. Although the selectivity coefficients frequently exceed unity for singly charged B species, the modifying effect of the square power term in the selectivity relation enhances the practical selectivity towards DQT.[7] Fig.2 summarizes selectivity data for (a) type 2 and (b) type 3 DQT ISEs. The reasons favouring NPPE and NPOE as recommended solvent mediators are clearly evident.

2.2 Paraquat Electrodes

Again, type 1 electrodes were of poor quality.[7] The responses of type 2 and type 3 electrodes are summarized in Table 4, while Fig.3 summarizes the selectivity characteristics for types 2 and 3 electrodes based on the favoured NPPE and NPOE solvent mediators.[7] It can be seen that the selectivity features are quite different (cf. Fig.2). The greater interference of PQT electrodes can arise from the elongated shape and longer $PQT^{2+}$ ion compared with $DQT^{2+}$ (Fig.1), and associated differences in electron distribution resulting from the wider separation of the charged nitrogen sites. Related



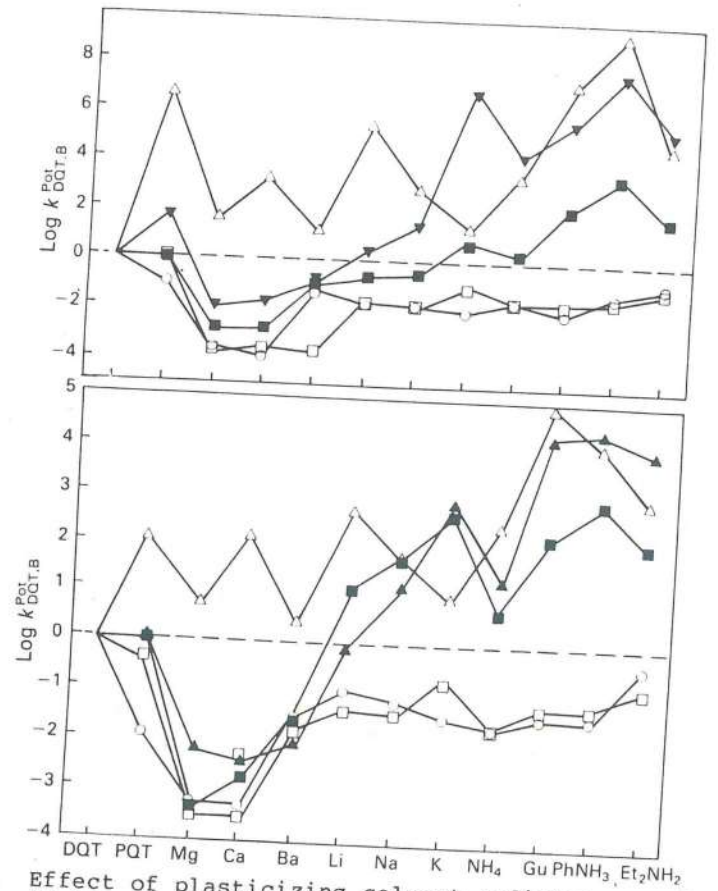


Fig.2 Effect of plasticizing solvent mediator on selectivity of type 2 (top) and type 3 (bottom) DQT ISEs. Key: o, NPOE; □ NPPE; △ DOPP; ▲ DNP; and ■, DBP. Lines joining points connect the same solvent mediator. (From Ref.7)

to these effects are the fact that type 3 PQT electrodes are of better quality than those of type 2 (Fig.3).

Fig.4 compares the calibrations of the PQT electrodes, based on NPPE solvent mediator, with the corresponding DQT ones.[7]

Table 4 Responses of electrodes for paraquat based on PQT.2TPB. Standard deviations in parentheses are for n = 4 spread over 48 h (from Ref.7)

| Electrode type and solvent mediator | | Parameter | | | |
|---|---|---|---|---|---|
| | | S/mV | C/mV | $a_{min}/10^{-6}$M | r |
| Type 2: | NPOE | 19.0 (0.8) | 82 (2.2) | 3.4 (4) | 0.999 |
| | NPPE | 27.1 (5.0) | 140 (30) | 9 (6) | 0.981 |
| Type 3: | NPOE | 30.1 (1.1) | 181 (18) | 1.2 (0.8) | 0.991 |
| | NPPE | 27.2 (4.0) | 155 (38) | 7 (12) | 0.989 |

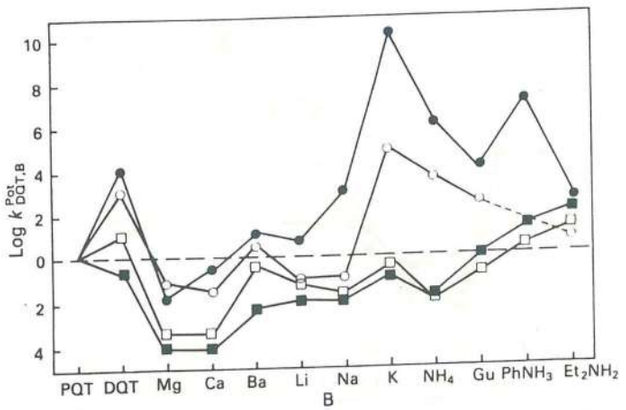


Fig.3 Selectivity of ISEs for PQT according to type and solvent mediators. (From Ref.7). Key: ●, NPOE and o, NPPE for type 2 electrodes; ■, NPOE and □, NPPE for type 3 electrodes.

## 3. DICATION (DIQUAT, PARAQUAT, AND 4,4'DIPYRIDINIUM) SENSING WITH A RANGE OF CROWN ETHERS

### 3.1 Diquat and Paraquat Electrodes

Dibenzo-30-crown-10 changes its shape dramatically to accommodate its guest molecules.[20] On the other hand, bis-paraphenylene-34-crown-10 hardly changes its shape



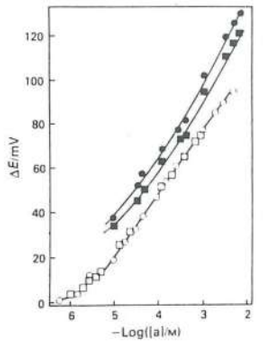


Fig.4 Responses of DQT and PQT electrodes (NPPE solvent mediator) towards DQT dibromide (for DQT) and PQT sulphate (for PQT). Key: o, type 2 (DQT); □, type 3 (DQT); ●, type 2 (PQT); ■, type 3 (PQT) (from Ref.7).

when it engulfs PQT. Hence, in order to determine whether this feature could promote ISE function for PQT, a wider range of crown ethers has been studied[15] for possible rôles as ISE sensors for PQT and DQT. Also, the structural analogue, 4,4'-DPy (Fig.1) has been included as analyte in order to complete the study.[15]

The six crown ethers selected for study[15] were dibenzo-30-crown-10 (DB30C10), bis-metaphenylene-32-crown-10 (BMP32C10), bis-metaphenylene-38-crown-12 (BMP38C12), bis-paraphenylene-34-crown-10 (BPP34C10), bis-paraphenylene-37-crown-11 (BPP37C11), and dinaphthalene-36-crown-10 (DN36C10). Dibutyl phthalate (DBP) and 2-nitrophenyl octyl ether (NPOE) were studied for their qualities as the associated solvent mediator.

It was not possible to discriminate between the different crown ethers for electrodes based on NPOE solvent mediator and treated with PQT dichloride, since

even electrodes with PVC membranes containing NPOE alone responded strongly to PQT.[20] Also, DBP-based electrodes gave relatively low PQT responses. These studies[20] suggest weak PQT complexation by the crown ethers. This is attributable to two effects. The first concerns the N-N separation in PQT (7.0Å) being dissimilar to the separations between the oxygens linked to aromatic rings (unlike the case of DQT discussed above for DB30C10), while the second weakening in complexation can arise from the reduced possibility for hydrogen bonding through the $CH_3$ groups attached to the PQT nitrogens compared with, say, 4,4'-DPy for which there is good ISE function.[15]

The weakness of the crown ether:PQT stability constants compared with that for $(DB30C10.DQT)^{2+}$ ($K_a$ = $1.8 \times 10^4$ $M^{-1}$, as given in Table 1) is notable. Thus, the $K_a$ data for $(BMP32C10.PQT)^{2+}$ and $(BPP34C10.PQT)^{2+}$ are just 760 $M^{-1}$ and 730 $M^{-1}$, respectively, and point to insufficient affinity by the crown ethers to ensure adequate ISE sensing.[15]

Again, comparing $K_a$ data for $(BMP3210.PQT)^{2+}$ (760 $M^{-1}$) and $(BMP32C10.DQT)^{2+}$ (390 $M^{-1}$) points to relatively poor ISE function for DQT. Indeed, in these studies,[15] the system based on DB30C10 was confirmed to be the best for DQT.

### 3.2 4,4'-Dipyridinium Electrodes

The generally good ISE response[15] towards 4,4'-DPy indicates that this may be a more favoured guest towards the crown ethers than is PQT. Furthermore, the last five-named crown ethers are more selective towards 4,4'-DPy than an electrode based on DB30C10 (see Table 5). Compared with PQT, replacement of the two



Table 5 Selectivity coefficient (log $k^{pot}_{4,4'-DPy,B}$) data for crown ether based electrodes for 4,4'-DPy (24-hr-old PVC electrodes based on crown ether and DBP solvent mediator and conditioned in 4,4'-DPy chloride) (From Ref.15)

| Ion(B) | Electrode No. (with crown ether) | | | | | |
|---|---|---|---|---|---|---|
| | 1 (DB30C10) | 2 (BMP32C10) | 3 (BMP38C12) | 4 (BPP34C10) | 5 (BPP37C11) | 6 (DN36C10) |
| $K^+$ | 4.2 | -0.36 | -0.22 | 0.51 | -0.23 | -0.70 |
| $NH_4^+$ | 3.2 | -0.40 | -1.0 | 0.08 | -1.0 | -0.81 |
| $Gu^+$ | 3.2 | -0.16 | -0.26 | 1.70 | -0.20 | -0.72 |
| $TMA^+$[a] | 1.4 | 1.6 | 1.0 | 1.74 | 1.0 | 0.7 |
| $Py^+$[a] | 1.0 | 1.4 | 1.2 | 2.2 | 0.9 | 1.2 |
| $Ba^{2+}$ | -1.2 | -3.5 | -2.7 | -2.6 | -2.7 | -2.93 |
| $DQT^{2+}$ | -1.8 | -1.85 | -2.4 | -0.5 | -2.4 | 02.72 |
| $PQT^{2+}$ | -1.7 | -1.82 | -2.5 | -2.4 | -2.8 | -2.14 |

[a] TMA = tetramethyl ammonium; $Py^+$ = pyridinium

1,1'-methyl groups with hydrogen (Fig.1) should provide better hydrogen-bonding sites. Also, hydrogen atoms are less bulky, and the aromatic rings in 4,4'-DPy should be more electron deficient, again favouring stronger interaction with the crown ethers under consideration to give good potentiometric response.[15]

Except for the DB30C10-based electrode, the selectivities of electrodes for 4,4'-DPy based on crown ethers[15] are superior to the electrodes[21] based on a simple ion-pair of 4,4'-DPy with TPB (discussed below). This lends support to strong complexation between 4,4'-DPy and BMP32C10, BMP38C12, BPP34C10, BPP37C11 and DN36C10.

## 4. ELECTRODES FOR GUANIDINIUM $[H_2N)_3C]^+$

The guanidinium cation [Gu] is eminently suitable for complexing with crown ethers through hydrogen bonds[16-18] and, as mentioned above, crown ethers of 27 members are the most selective to guanidinium. The stability trend for the complexes with various ions is K > Gu > alkylammonium > metal ions. An electrode system based on DB27C9 using dibutyl phthalate plasticizer in PVC[22] has been studied at greater length and compared with electrodes based on tetraphenylborate (TPB).[23]

Electrodes involving DB27C9 sensor with various plasticizing solvent mediators were best when the solvent mediator was dibutyl phthalate, dioctyl adipate or dioctyl sebacate, with the phthalate being preferred.[23] Those based on 2-nitrophenyl phenyl ether and 2-nitrophenyl octyl ether were rather slower in response, while DOPP-based electrodes were noisy with poor response.[23] The addition of GuTPB (TPB is an anion



excluder) does not improve sensitivity but, instead, worsens both linear range and detection range compared with electrodes from PVC membranes containing plasticizer and DB27C9 alone (Table 6).[23] However, selectivity of Gu over potassium is best for electrodes with added GuTPB (Table 7).

Table 6 Response characteristics of five types (see footnote) of guanidinium electrodes based on DB27C9 and GuTPB. (From Ref.23)

| Electrode type [a] | Slope/mV decade$^{-1}$ (n=3) | Linear range /mM | Detection limit /μM | Resistance /MΩ | Correlation coefficient r |
|---|---|---|---|---|---|
| 1 | 58(±0.5) | 0.1-100 | 30 | 25 | 0.998 |
| 2 | 52(+1) | 0.6-100 | 160 | 3 | 0.985 |
| 3 | 53(±1) | 0.5-100 | 100 | 3 | 0.981 |
| 4 | 55(±0.5) | 0.1-100 | 50 | 5 | 0.991 |
| 5 | 60(±0.5) | 0.05-100 | 10 | 0.1 | 0.998 |

[a] Composition of PVC (150 mg) membranes of electrodes 1 to 5 containing 300 mg dibutyl phthalate (except for membrane 5 with 360 mg of dioctyl phenyl phosphonate):

| Membrane No. | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| DB27C9/mg | 5 | 5 | 5 | - | - |
| GuTPB/mg | - | 5 | 10 | 10 | 40 |

Electrodes based on GuTPB alone with DBP as plasticizing solvent mediator gave good responses and good selectivity towards Gu over metal ions, but there was better all-round selectivity[23] when dioctylphenyl phosphonate was used as a solvent mediator. However, the TPB-based electrodes were more sluggish in response.[23]

Table 8 Estimates of $K_s^{-1}$ (inverse solubility product) for TPB precipitates with a range of cations (from Ref.21)

| Ion | $K_s^{-1}$ * | $K_s^{-1}$ * |
|---|---|---|
| $NH^+$ | 5.6(4.3) x $10^6$ | 1.2 x $10^7$ |
| $K^+$ | 2.8(1.3) x $10^7$ | 4.2 x $10^7$ |
| $Rb^+$ | 1.2(0.43) x $10^8$ | 5 to 20 x $10^8$ |
| $Cs^+$ | 1.1(1.1) x $10^7$ | 1.2 x $10^7$ |
| | 3.3 x $10^9$ | |
| 4,4-$DPy^{2+}$ | 6(1.8) x $10^{10}$ | - |
| | 1.5 x $10^{11}$ £'d | |
| $DQT^{2+}$ | 4(4.5) x $10^{17}$ | - |
| | 2.4 x $10^{13}$ £ | |
| | 1.1(0.36) x 10j$^5$É | |
| $PQT^{2+}$ | 1.1(1.7) x $10^{12}$ | - |
| | 3.2 x $10^{16}$ £ | |
| | 7.7(9.2) x $10^{15}$ £ | |

a Observed values, means of 3-8 experiments. Standard deviations are given in parentheses.
b Literature values of $K_s^{-1}$.
c Largest $K_i$ values observed.
d Values determined in 0.2M sodium chloride solution.

for PQT transfer at a water-nitrobenzene interface. The free energy term, $\Delta G_t^{\circ}$ is the combined free-energy change for the transfer of ion pairs. The last column in Table 9 estimates the a(min) for $DQT(TBP)_2$/ $PQT(TPB)_2$ and 4,4'-DPy from the equation

$$a(min) = (0.25/K_2)^{*3} \qquad (4)$$

in a similar way to the calculation of $[Ba^{2+}]$, from $(0.25\ Ks)^{1/3}$, existing in equilibrium with a 2:1 salt as in barium iodate.[21] These data (last column of Table 9) were then compared[21] with experimental values in Table 10 which summarizes the response characteristics of ISEs for DQT, PQT and 4,4'-DPy, and the agreement is reasonable.

Pic, however, is not sufficiently lipophilic to form the basis of a functional ISE for the dications.[21] ISEs with T4C1PB as the sensor show the best sensitivity for DQT (30 nM) or PQT (200 nM). These compare with a minimum of 200 nM for PQT determined by ion-pair extraction-spectrophotometry.[21] However, the same improvement does not extend to 4,4'-DPy ISEs.

Table 9 Calculation of TPB ion-pair extraction constants ($K_2$) for a range of ions (for full details see Ref.21)

| Ion | $\Delta G_t^{\circ}$ | $\Delta G_i^{\circ}$ | $K_{ext}$ | $K_2$ | a(min)/$10^{-6}$M |
|---|---|---|---|---|---|
| $NH^+$ | 26.8 | -9.1 | 253 | 1.4x$10^9$ | 27 |
| $K^+$ | 23.9 | -12 | 128 | 3.6x$10^9$ | 16 6 |
| $Rb^+$ | 19.4 | -16.5 | 785 | 1.8x$10^{12}$ | 0 7 |
| $Cs^+$ | 15.4 | -20.5 | 3950 | 1.3x$10^{13}$ | 0 3 |
| $DQT^{2+}$ | 49 | -22.8 | 1x10^ | 4x$10^{16}$ | 1 8 |
| | | | | (1.1x$10^{19}$) | (0 3) |
| $PQT^{2+}$ | 49 | -22.8 | 1x$10^4$ | 1.1x$10^{16}$ | 2 8 |
| | | | | (8x$10^{20}$) | (0 07) |
| $PQT^{2+}$ | 49 | 13.1 | 5x$10^3$ | 9x$10^8$ | 652 |
| 4,4-$DPy^{2+}$ | 53.5 | -18.3 | 1624 | 9.7x1,;$^3$ | 14 |
| | | | | (2.4x$10^{11}$) | (1 0) |

Table 10 Response characteristics of ISEs for DQT, PQT and 4,4'-DPy. Mean with S.D. in parentheses: 1 to 9 calibrations for 24-72 h old electrodes based on NPOE solvent mediator (from Ref.21)

| Ion-pair molecules | Electrode parameter | | | |
|---|---|---|---|---|
| | S/mV/log a | C/mV | a(min)/$10^{-6}$M | r * |
| $DQT(PF_6)_2$ | 27 (14) | 151(11) | 4(3) | 0.999 |
| $DQT(TPB)_2$ | 28(0.6) | 161 (2.3) | 1.6(0.8) | 0.999 |
| $PQT(TPB)_2$ | 28(2) | 154(16) | 1.2(0.6) | 0 999 |
| 4,4'-$DPy(TPB)_2$ | 29(4) | 150(18) | 7(1) | 0 996 |
| $DQT(T4C1PB)_2$ | 32(1.5) | 244(13) | 0.03(0.006) | 0 997 |
| $PQT(T4C1PB)_2$ | 29(0.1) | 196(3) | 0.2(0.05) | 0 999 |
| 4,4'-$DPy(T4ClPB)_2$ | 46(4) | 238{17) | 11(10) | 0,988 |

Correlation coefficient

## 6. CONCLUSION

Good PVC matrix membrane ISEs can be modelled on crown ether sensors for the herbicidal diquat and paraquat dications and the pharmaceutically important guanidinium cation. Generally, there is some agreement between stability (association) constant data and quality of ion-sensor, and it is emphasized that the association is sufficiently strong (but not too strong) for the sensing to occur. The rôle of the anion excluder still demands further attention since, in this case, as in others, the excluder itself is electrochemically active. Nevertheless, there are interesting trends between electrode function and ion-pair extraction.

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# MECHANISM OF THE REDUCTION OF Ni(II)-ALCOHOLAMINE COMPLEXES ON THE DROPPING MERCURY ELECTRODE

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## ABSTRACT

The polarographic characteristics of the Ni(II) ion in presence of the four aminoalcohols monoethanolamine, N-methylethanolamine, N-ethylethanolamine and N,N-dimethylethanolamine are reported. In general, half-wave potentials for the complexes are more positive than for the aquo-ion, and shift towards more negative values as the concentration of ligand increases. Transfer coefficients, $\alpha$, electrode reactions rates and activation energies were determined for the reduction of the complexes. Differences between the reduction mechanism of the various Ni(II)- aminoalcohol complexes are pointed out.

## INTRODUCTION

The unusual electrochemical behaviour exhibited at the dropping mercury electrode by complexes of Ni(II) with nitrogen bearing ligands, which has long been known, has recently been the subject of a number of articles (1-4). As far as we know, however, there has been only one study (5) of the electrochemical behaviour of Ni(II)-alcoholamine complexes, and only a qualitative description was given. The present article reports quantitative electrochemical