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Acid Red 88 Dye Anion-Selective Electrode

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ABSTRACT

An ion-selective membrane electrode selective to the Acid Red 88 (C.I. 15620) dye anion has been constructed. This electrode, with the Acid Red 88 dye anion–cetylpyridinium cation carrier complex incorporated within a poly(vinyl chloride) gel membrane, permits direct determination of the dye monomer concentration. In this work its fabrication, general performance and selectivity are described. The selectivities have been obtained by a mixed solution method for the Acid Orange 7 (C.I. 15510), Acid Red 13 (C.I. 16045) and Acid Blue 25 (C.I. 62055) interfering anions. The selectivity coefficients suggest that the dye electrode is not sensitive to interfering dye anions of similar structure and different charge or size.

1 INTRODUCTION

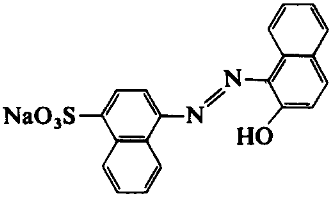
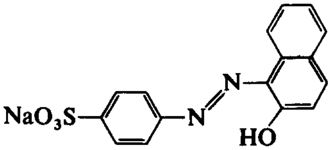
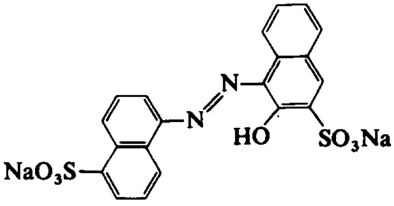
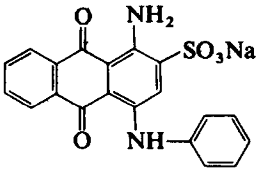
During recent years, ion-selective membrane electrodes selective to cations, anions and to other species have been made and used for a variety of analytical applications.[1–14] We have constructed an ion-selective membrane electrode selective to a dye anion. The membrane used in this electrode has been made by incorporating a dye anion–surfactant cation carrier complex into a poly(vinyl chloride) matrix. The preparation and fundamental electrochemical properties of the dye electrode and its behaviour in the presence of different interfering dye anions are described in the paper. The selectivity of the dye electrode was checked by a mixed solution method. Two different uni- and one divalent acid dyes were chosen as interferent species.

2 EXPERIMENTAL

2.1 Materials

All dyes used in this work were synthesized[15] and then purified by repeated recrystallization from aqueous acetone solution and from the *N*,*N'*-dimethylformamide-benzene. Table 1 lists the dyes, their structure and molecular weights. *N*-Cetylpyridinium chloride (CPC); Kemika, Zagreb, Croatia) was purified by repeated recrystallization from acetone. Poly(vinyl chloride) (PVC; Solvic, Belgium) was purified by extraction with methanol. Dioctylphthalate (DOP; Ipranol O, Iplas, Koper,

TABLE 1
Dyes Investigated

Dye	*Molecular weight* ($g\ mol^{-1}$)	*Structure*
Acid Red 88	399·9	
Acid Orange 7	350·3	
Acid Red 13	502·0	
Acid Blue 25	416·3	

Slovenia) and tetrahydrofuran (THF; Kemika, Zagreb, Croatia) were of analytical grade. All solutions were prepared in triple-distilled water.

2.2 Preparation of the dye electrode[4,6]

A non-polymeric ion-exchange complex was prepared by mixing equimolar amounts of hot solutions of the mono-azo acid dye Acid Red 88 and CPC. A precipitate, insoluble in water, formed immediately. It was washed with distilled water and dried. A 0·005 g sample of this complex, 0·35 g of PVC and 1·15 g of DOP were then dissolved in 6 ml THF and filtered through a 1·2 μm millipore filter and cast on a clean glass plate set horizontally (diameter 60 mm). This solution was left for 2 days to allow the THF to evaporate. The dry membrane was kept under vacuum at 30°C for 24 h. A disc of the required size was cut from this membrane and mounted in the electrode body (PVC tube). The internal reference solution was a 1×10^{-4} M solution of Acid Red 88. Before use, the dye electrode was soaked in 1×10^{-4} M Acid Red 88 dye solution for 1 day.

2.3 Apparatus and general measurement procedure

$$\begin{array}{l}
\mathrm{Hg}\,|\,\mathrm{Hg_2Cl_2}\,|\,\mathrm{KCl(satd)}\,\|\,\text{test solution}\,|\,\text{polymer membrane}\,|\,\text{internal solution}\,\|\,\mathrm{KCl(satd)}\,|\,\mathrm{Hg_2Cl_2}\,|\,\mathrm{Hg} \\
\qquad\qquad \mathrm{Na^+D^-(B^- = D^-)} \quad + \mathrm{CPC^+D^-(B^- = D^-)} \quad \mathrm{Na^+D^-(B^- = D^-)} \\
\qquad\qquad \times\ \mathrm{mol\,dm^{-3}} \qquad\qquad\qquad\qquad\qquad 1 \times 10^{-4}\,\mathrm{mol\,dm^{-3}}
\end{array}$$

where D^- is the dye anion.

Measurements were taken with the above-presented electrochemical cell using a Model PHM 26 Radiometer pH-meter. The electrode was tested against the reference calomel electrode (Model HEK 0301, Iskra, Slovenia) via an ammonium nitrate salt bridge. In all experiments the temperature was controlled to within ±0·1°C by circulation of thermostatted water through a double glass cell and the sample solution was continuously stirred using a magnetic stirrer. During the e.m.f. measurements the concentration of the test sample solutions was changed successively by adding known amounts of solution of known concentration to the initial test solution from a micrometer burette.

The potentiometric selectivity coefficients were evaluated by a mixed solution method.[16,17] In the mixed solution method, the electrode potentials were measured in solutions containing a fixed amount of interferent ion with varying concentrations of primary ion, for which the electrode was designed. The response of the electrode was tested in the concentration range 10^{-7} to 10^{-3} mol dm^{-3} at 25°C. Plots of measured potential versus logarithm of activity were created for a series of concentrations of the Acid Red 88 solution containing a constant amount ($4{\cdot}9 \times 10^{-5}$ M,

$1{\cdot}0 \times 10^{-4}$ M, $3{\cdot}9 \times 10^{-4}$ M, $9{\cdot}9 \times 10^{-4}$ M) of Acid Orange 7, ($1{\cdot}1 \times 10^{-5}$ M, $1{\cdot}0 \times 10^{-4}$ M, $1{\cdot}2 \times 10^{-3}$ M) of Acid Red 13 and ($1{\cdot}2 \times 10^{-6}$ M, $5{\cdot}1 \times 10^{-6}$ M, $1{\cdot}1 \times 10^{-5}$ M, $1{\cdot}2 \times 10^{-4}$ M) of Acid Blue 25 anions.

3 RESULTS AND DISCUSSION

3.1 Calibration of the dye electrode

The PVC dye electrode was calibrated in pure Acid Red 88 solution of concentration increasing from 10^{-7} M to 10^{-3} M Acid Red 88 at 25°C. Concentrations were converted into activities using Guggenheim's expression:[18]

$$-\log f = Az^2 \frac{\sqrt{I}}{1 + \sqrt{I}} \qquad (1)$$

where f and z are the activity coefficient and ionic charge of the Acid Red 88 ion, respectively, $A = 0{\cdot}5115$ mol$^{-1/2}$ dm$^{3/2}$ at 25°C and I is the ionic strength of the solution. The e.m.f. of the cell (E) as a function of Acid Red 88 activity (log a) is shown in Fig. 1. The e.m.f. response was

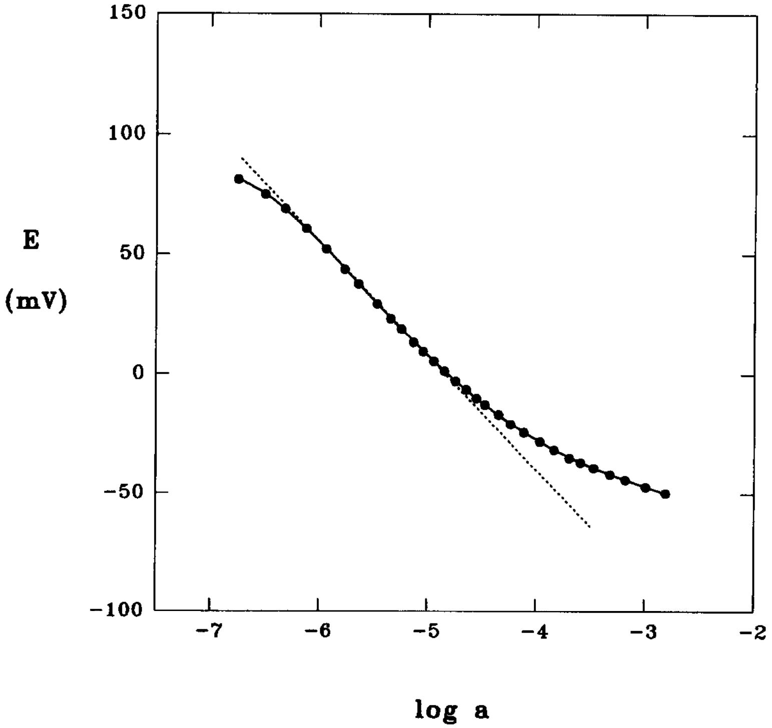


Fig. 1. Calibration of the Acid Red 88 dye anion-selective electrode at pH 6 ± 0·2 and 25°C. (Gradient is −47·8 mV per activity decade.)

found to be linear over the activity range $7{\cdot}5 \times 10^{-7}$ M to $1{\cdot}4 \times 10^{-4}$ M Acid Red 88, with a gradient of −47·8 mV per activity decade at 25°C. The calibration gradient of the dye electrode remained constant within 1·2 mV per decade over a period of 3 months. From Fig. 1 it is evident that there are two deviations from linear behaviour, one at low and one at high dye concentrations. The first deviation is due to the detection limit of the ion-selective electrode, which depends also upon the interfering ion concentration in the sample,[19] while the second deviation is due to the dye aggregation.[20] Because of dye aggregation, the fraction of monomers decreases with increasing concentration, and the measured e.m.f. values start to deviate from the theoretical straight line. The response times of the dye electrode decrease as the Acid Red 88 activity increases from a few minutes at high activities to approximately 15 min at low activities. The dye electrode was still functioning after 6 months without any serious deterioration in response times or deviation from linearity.

3.2 Interferences

The selectivity coefficients indicate the extent to which foreign ions interfere with an electrode's normal response to primary ions. The selectivity coefficient K_{ij}^{pot} of the dye (I) electrode towards another dye (J) as interferent ion is defined by the Nikolsky equation[21,22] as follows:

$$E = E^0 - \frac{k}{z_i} \log \left(a_i + K_{ij}^{\mathrm{pot}} a_j^{z_i/z_j}\right) \tag{2}$$

where E^0 is the standard potential of the electrode, z_i and z_j are the activities of the ions i and j and K_{ij}^{pot} is the selectivity coefficient of the electrode in the presence of the ion j. Several methods are available for determining this selectivity coefficient.[16,17,22] The most realistic approach to the selectivity problem is to take the potentials in mixed solutions containing both the primary i ions and the interfering j ions. Therefore, only the mixed solution method has been followed in this study. E.m.f. measurements have been made for the series of solutions containing a fixed amount of interferent dye anion, but variable Acid Red 88 dye concentrations. The selectivities of the Acid Red 88-selective dye electrode to the Acid Orange 7 and Acid Red 13 anions are shown in Figs 2 and 3, respectively. As the activity of the primary Acid Red 88 anion decreases, there is a gradual onset of interference until, at a high enough concentration of interferent Acid Orange 7 or Acid Red 13 ion, a complete interference is reached. In other words, the electrode response starts deviating from linearity as the concentration ratio of the interfering ion is increased and eventually becomes independent of the activity of the

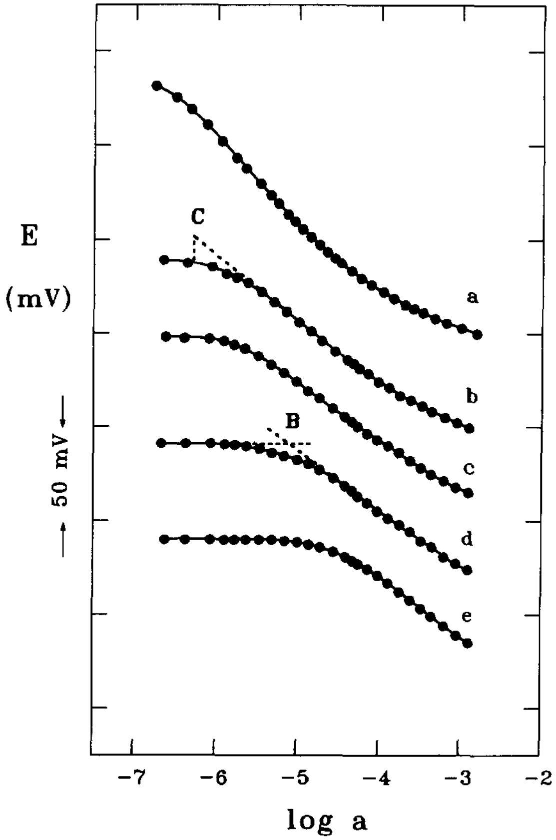


Fig. 2. Potential response of the Acid Red 88 dye anion-selective electrode to the change of the primary anion activity in four mixed Acid Red 88–Acid Orange 7 solutions at 25°C. **a**: Calibration graph, Acid Red 88 only; **b**: $4{\cdot}9\times10^{-5}$ M Acid Orange 7; **c**: $1{\cdot}0\times10^{-4}$ M Acid Orange 7; **d**: $3{\cdot}9\times10^{-4}$ M Acid Orange 7; **e**: $9{\cdot}9\times10^{-4}$ M Acid Orange 7.

primary ion. The intercept (Fig. 2, point B) of the extrapolated linear response line, which can be presented as

$$E = E^0 - \frac{k}{z_i} \log a_i \tag{3}$$

with that of the horizontal total interference, presented as

$$E = E^0 - \frac{k}{z_i} \log (K_{ij}^{\text{pot}} a_j^{z_i/z_j});\ a_j = \text{const.} \tag{4}$$

defines the activity of the primary ion $(a_i)_\text{B}$ at which the selectivity coefficient K_{ij}^{pot} is given as

$$K_{ij}^{\text{pot}} = \frac{(a_i)_B}{a_j^{z_i/z_j}} \tag{5}$$

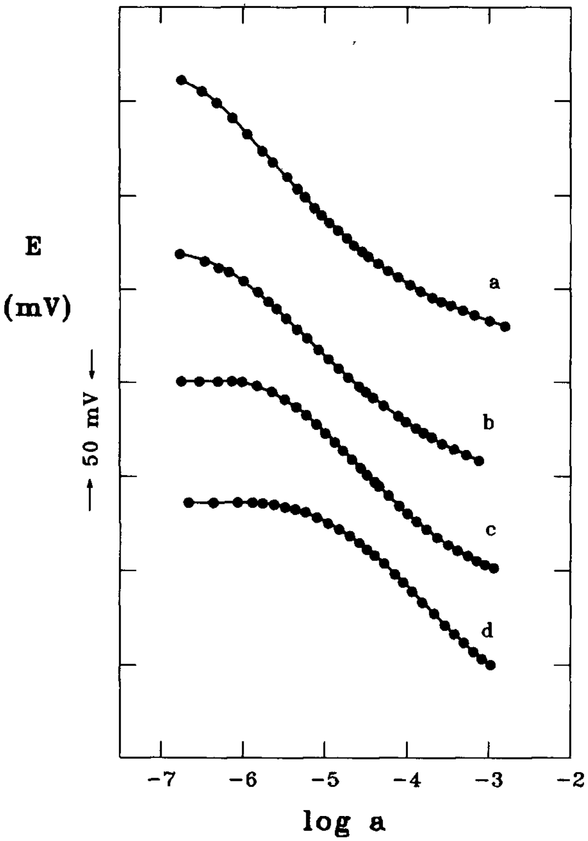


Fig. 3. Potential response of the Acid Red 88 dye anion-selective electrode to the change of the primary anion activity in three mixed Acid Red 88–Acid Red 13 solutions at 25°C. **a**: Calibration graph, Acid Red 88 only; **b**: $1{\cdot}1\times10^{-5}$ M Acid Red 13; **c**: $1{\cdot}0\times10^{-4}$ M Acid Red 13; **d**: $2{\cdot}1\times10^{-3}$ M Acid Red 13.

When at a given activity of the interferent ion a_j it is not possible to establish the zero response line experimentally (Fig. 2, curves b and c), the selectivity coefficient K_{ij}^{pot} is obtained from

$$K_{ij}^{\text{pot}} = \frac{(a_i)_C}{(a_j)^{z_i/z_j}} \qquad (6)$$

where $(a_i)_C$ is the activity of the primary ion obtained by extrapolating the linear slope (eqn (3)) to a point (k/z_i) log 2 or $14{\cdot}4/z_i$ mV, in our case, above the mixed response line (eqn (2)) where $(a_i)_C = K_{ij}^{\text{pot}} a_j^{z_i/z_j}$ (Fig. 2, point C). Using these two procedures the selectivity coefficients K_{ij}^{pot} of the Red 88-selective electrode were determined for Acid Orange 7 and Acid Red 13 interferent ions from the measured E versus log a_i curves (Figs 2 and 3). These values are much smaller than unity over the whole measured activity range (Table 2), which means that the Acid Red 88-selective electrode is significantly more sensitive to primary Acid Red 88 ions than to interferent Acid Orange 7 or Acid Red 13 ions.

The results presented in Table 2 also indicate that the dye electrode suffers minimum interference when the interfering dye anion is of similar structure and different size or doubly charged. The low values of selectivity coefficients obtained for doubly charged Acid Red 13, whose structure differs only in one sulphonic group from the Acid Red 88 structure, indicate that the Acid Red 88-selective dye electrode is not sensitive to doubly charged dimers and highly charged multimers of the dye Acid Red 88. This observation leads to an important conclusion that this dye electrode permits a direct determination of the dye monomer concentration at a given total dye concentration, which is useful for studying the aggregation process of a dye in aqueous solution. In Fig. 4 the interfering effect of Acid Blue 25 ions on the Acid Red 88-sensitive electrode is shown. The shape of the e.m.f. response curves suggests that the studied dye electrode is more sensitive to the interfering Acid Blue 25 anions than to the primary Acid Red 88 anions. According to this, K_{ij}^{pot} values are greater than unity over the measured concentration range 4×10^{-6} to 1×10^{-4} M Acid Blue 25 (Table 2). This observation indicates that the structure of interferent ions most probably plays an important role in determining the selectivity coefficients and therefore the usefulness of the PVC-membrane electrodes selective to specific dye ions.

TABLE 2

The Selectivity Coefficients, K_{ij}^{pot} of Acid Red 88-Selective Dye Electrode Determined at 25°C in Mixed Solutions Containing Acid Red 88 and Interfering Anions

Interfering anion j	*Concentration of interfering anion j (mol dm^{-3})*	*Selectivity coefficient, K_{ij}^{pot}*	
		From intercept	*From 14·4/z_i*
Acid Orange 7	$4{\cdot}9\times10^{-5}$	—	0·009
	$1{\cdot}0\times10^{-4}$	—	0·006
	$3{\cdot}9\times10^{-4}$	0·022	—
	$9{\cdot}9\times10^{-4}$	0·025	—
Acid Red 13	$1{\cdot}1\times10^{-5}$	—	0·000 08
	$1{\cdot}0\times10^{-4}$	0·000 2	—
	$1{\cdot}2\times10^{-3}$	0·000 3	—
Acid Blue 25	$1{\cdot}2\times10^{-6}$	—	0·418
	$5{\cdot}1\times10^{-6}$	3·284	—
	$1{\cdot}1\times10^{-5}$	3·643	—
	$1{\cdot}2\times10^{-4}$	≈50	—

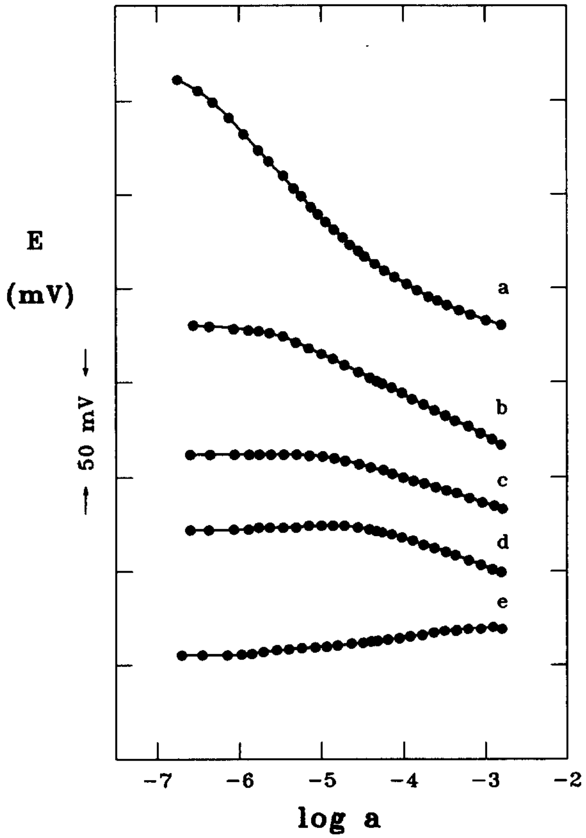


Fig. 4. Potential response of the Acid Red 88 dye anion-selective electrode to the change of the primary anion activity in four mixed Acid Red 88–Acid Red 25 solutions at 25°C. **a**: Calibration graph, Acid Red 88 only; **b**: $1{\cdot}2\times10^{-6}$ M Acid Blue 25; **c**: $5{\cdot}1\times10^{-6}$ M Acid Blue 25; **d**: $1{\cdot}1\times10^{-5}$ M Acid Blue 25; **e**: $1{\cdot}2\times10^{-4}$ M Acid Blue 25.

4 CONCLUSION

The general performance of the Acid Red 88-selective electrode shows that it could be used as a commercial electrode. The selectivity coefficients for three interferent dye anions suggest that the dye electrode is not sensitive to interfering anions which have similar structure and different size or doubly charged. The dye electrode is also insensitive to dimers and higher multimers of the dye investigated. This means that the dye electrode permits a direct determination of the dye monomer concentration, which is useful for studying the dye aggregation. On the basis of the measured dye monomer concentration at a given total dye concentration and at different temperatures, the dimerization constants K_D and the corresponding thermodynamic functions ΔG_D, ΔS_D and ΔH_D can be determined. Using an appropriate stepwise association model, one can even estimate the concentrations of higher multimers.[20]

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