

ION SELECTIVE SENSORS*

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ABSTRACT

An account is given of ion selective sensors. Glass membrane-, solid-state membrane-, and liquid-membrane electrodes are all considered.

Ion selective sensors are electrode devices which selectively measure the activity of one given ion or of a series of such ions in an aqueous or non-aqueous solution of different ions†. Basically, different types of electrodes may be used but the analytically most attractive ones seem to be the membrane electrodes. *Figure 1* shows a schematic diagram of such a cell assembly. There are three fundamentally different types of membrane which selectively interact with the ion or ions to be determined:

- (1) glass membrane
- (2) solid-state membrane: (a) homogeneous solid-state membrane
(b) heterogeneous solid-state membrane
- (3) liquid membrane: (a) electrically charged ligand groups (ion exchangers) as membrane components
(b) electrically neutral ligand groups as membrane components

The sensors used in routine applications are normally a combination of an inner reference electrode (internal reference electrode), an inner (internal) filling solution and an ion selective membrane, all housed in one casing. Examples of such units are shown in *Figure 2* for the types of membrane above-mentioned.

In the glass electrode [*Figure 2(a)*]⁴, the ion selective membrane is usually fused to an inert glass stem, while in solid-state membrane electrodes⁷ it is normally cemented to an inert membrane shaft [*Figures 2(c), (d)*]. For

* Augmented summary of a lecture delivered at the Third Analytical Chemistry Conference, Budapest, August 1970.

† Several recent review articles¹⁻⁶ list a large number of publications related to ion-selective electrode systems.

heterogeneous solid-state membranes, Pungor *et al.*³ use about 30 to 50 wt % of ion-selective membrane component (e.g. silver halide) having a grain size of 5 to 10 μm in a silicone rubber matrix.

In the liquid membrane electrode of *Figure 2(b)*^{7,8}, a filter paper impregnated with ion selective ligand acts as the membrane. Any ion selective component diffusing into and thus contaminating the solution being measured is replaced from the reservoir 5 (*Figure 2(b)*); this should ensure a long electrode life of the membrane electrode system⁸.

For ease of handling of the cell assembly and for working with small samples, it is advisable to combine the ion selective membrane with the inner reference electrode, the internal filling solution, and the reference electrode that dips into the solution to be measured to form a single structural unit (single-rod cell assembly, combination electrode) (see literature cited in ref. 2).

Under conditions which are discussed in detail elsewhere^{2,9}, the response of an ion selective sensor to N different monovalent ions is given as

$$\text{EMF}(T) = E_0^A + (RT/F) \ln \sum_{i=1}^N K_{1i}^{\text{Pot}} a_i \quad (1)$$

where $\text{EMF}(T)$ is the EMF of the cell assembly at the absolute temperature T , F is the Faraday constant, a_i are ion activities in the sample solution, E_0^A is a parameter dependent on T , R is the gas constant, and K_{1i}^{Pot} is a selectivity constant (preference of sensor for ion i over ion 1). For glass membranes and solid-state ion-exchange membranes the selectivity constant K_{ij}^{Pot} , which characterizes the preference of the sensor for the ion j as compared with the ion i , is given by

$$K_{ij}^{\text{Pot}} = (u_j/u_i) K_{ij} \quad (2)$$

where K_{ij} is the equilibrium constant of the exchange



and u_i and u_j are the mobilities of the ions in the membrane. If the sensor responds to a bivalent ion (a_1) and a monovalent ion (a_2) we get

$$\text{EMF}(T) = E_0^B(T) + (RT/2F) \ln (a_1 + K_{12}^{\text{Pot}} a_2^2) \quad (4)$$

If there were no interfering ions, the sensor would show a linear change in EMF as a function of $\log a_i$. This holds to a very high degree for pH responsive glass electrodes, which are by far the most selective and specific sensors known to date, exhibiting selectivities¹⁰ of H_3O^+ over alkali metal ions X^+ of up to at least 10^{13} and a linear response in $\log a_{\text{H}_3\text{O}^+}$ over a concentration range of 14 orders of magnitude (see *Figure 3*¹¹). For good pH electrode glasses in aqueous solutions of alkali hydroxides, deviations from linearity become significant¹⁰ only at pH values above approximately 13

$$\text{EMF}(T) = E_0^C + (2.303 RT/F) \log (a_{\text{H}_3\text{O}^+} + 10^{-13} a_{\text{X}^+}) \quad (5)$$

The correction term $10^{-13} a_{\text{X}^+}$, due to the alkali cation X^+ , is treated as an interference which may, however, become the dominant term in aprotic and basic non-aqueous solvent systems where $a_{\text{H}_3\text{O}^+}$ is small¹⁰ compared to $K_{\text{H}_3\text{O}^+\text{X}}^{\text{Pot}} a_{\text{X}^+}$.

By modifying the glass composition, it is possible to produce glass electrodes possessing a usable response for Na^+ , K^+ , Ag^+ and other cations⁴. Thus electrodes with selectivities of Na^+ over H_3O^+ of 7.8 ($K_{\text{Na}^+/\text{H}_3\text{O}^+}^{\text{Pot}} = 0.13$) and of Na^+ over K^+ of 7.2×10^3 ($K_{\text{Na}^+/\text{K}^+}^{\text{Pot}} = 1.4 \times 10^{-4}$) have been prepared¹². Unfortunately, the selectivities of K^+ over Na^+ of around ten so far obtained in glass electrodes of analytical applicability are rather poor ($K_{\text{K}^+/\text{Na}^+}^{\text{Pot}} \sim 0.1$)^{4,13}. Due to the low relative mobility of polyvalent ions in

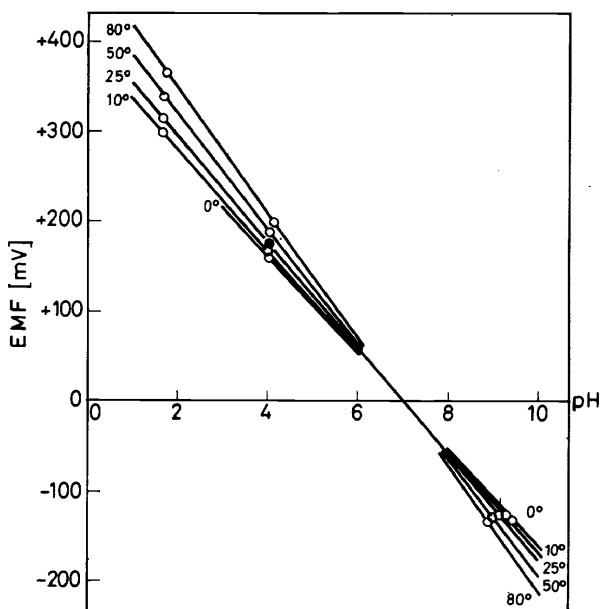


Figure 3. Response of a pH glass electrode cell assembly¹¹. (The points correspond to experimental data. The straight lines have been drawn assuming a theoretical response to $a_{\text{H}_3\text{O}^+}$ and an isopotential pH of 7.0).

glass membranes it is unlikely that glass compositions displaying a high selectivity for polyvalent ions will ever be found^{4,2}. Theoretical considerations nourish the expectation that homogeneous and heterogeneous silver halide membranes featuring AgCl , AgBr and AgI as active membrane components should respond in a similar manner to the halide ions Cl^- , Br^- and I^- respectively. This is indeed so^{2,3}. Furthermore, their response is not unlike the one found with silver-silver halide electrodes (electrodes of the second kind) as towards halide ions.

Deviations are found mainly with redox systems. The main advantage of the silver halide solid-state membrane electrodes over the silver-silver halide electrodes is that the former is less sensitive to redox systems.

Apart from pH measurement a total of so far about 300 papers deal with more or less selective detection of about 40 ions and components (for review, see ref. 2). However, only a relatively small number of sensors have found general analytical application. Glass electrodes (often having the

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composition NAS_{11-18} or NAS_{27-4}) are normally used for the determination of sodium and potassium ions^{4,5}, and the following electrodes have found rather general acceptance:

solid-state membrane electrodes (ion detected/membrane component):

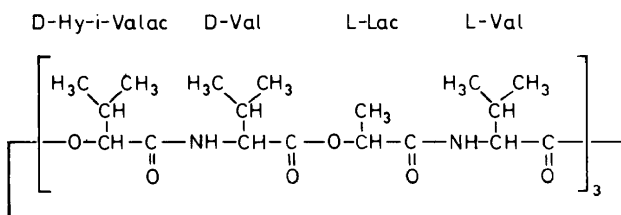
F^-/LaF_3 ¹⁴; Cl^-/AgCl ; Br^-/AgBr ; I^-/AgI ; $\text{S}^{2-}/\text{Ag}_2\text{S}$;
 Ag^+/AgI or Ag_2S ; CN^-/AgI ; $\text{Cu}^{2+}/\text{CuS}$, Ag_2S mixed crystal¹⁵;
 $\text{Pb}^{2+}/\text{PbS}$, Ag_2S mixed crystal¹⁵.

liquid membrane electrodes:

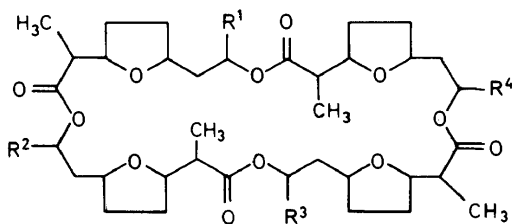
Ca^{2+} ⁷, $\text{Ca}^{2+} + \text{Mg}^{2+}$ (for water hardness)
 NO_3^- ⁷, K^+ ¹⁶.

Manufacturers often designate electrodes according to the ions for which they are supposed to be used. These designations should not be taken too seriously. So-called 'calcium electrodes' (liquid membrane electrodes) prefer Zn^{2+} ^{17,2}. Before using such electrode systems it is therefore advisable to study the corresponding selectivity constants carefully.

Valinomycin



Macrotetrolides



$\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{CH}_3$	Nonactin
$\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{CH}_3$	$\text{R}^4 = \text{C}_2\text{H}_5$ Monactin
$\text{R}^1 = \text{R}^3 = \text{CH}_3$	$\text{R}^2 = \text{R}^4 = \text{C}_2\text{H}_5$ Dinactin
$\text{R}^1 = \text{CH}_3$	$\text{R}^2 = \text{R}^3 = \text{R}^4 = \text{C}_2\text{H}_5$ Trinactin

Figure 4. Structures of valinomycin and the macrotetrolide antibiotics.

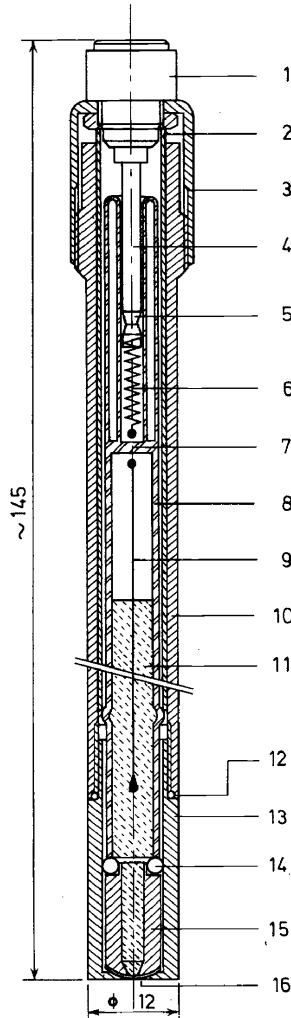


Figure 5. Liquid membrane sensor. 1: Plug for inner reference electrode system and electrical screening; 2: screening; 3: metal cap; 4: contact pin; 5: silver contact; 6: metal spring; 7: platinum duct; 8: glass insert; 9: inner reference electrode; 10: electrode shaft (plastic); 11: internal filling solution; 12: O ring; 13: membrane support (plastic); 14: O ring; 15: hollow cylinder (plastic) pressing on membrane 16; 16: liquid membrane (filter paper impregnated with ion selective ligand). The membrane 16 is fixed by the hollow cylinder 15 and the O ring 14. This is done by screwing 3 firmly on to 10 by the screening 2 and the glass insert 8.

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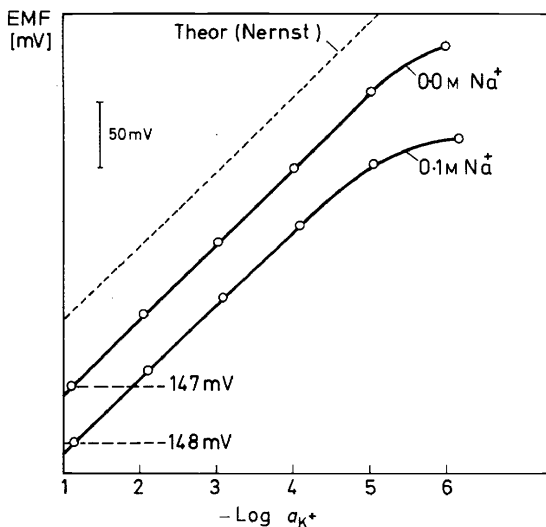


Figure 6. Electrode function of a liquid membrane sensor using valinomycin in diphenyl ether¹⁶.

Liquid membrane electrodes of the electrically neutral ligand type with considerably higher selectivities for K^+ over Na^+ than are obtained with glass electrodes can be produced with the aid of certain antibiotics that selectively complex K^+ ^{2, 16, 18}. Thus valinomycin (Figure 4) dissolved in diphenyl ether applied on to Millipore filter* furnishes liquid membrane

Table 1. Selectivity $K_{K^+M^+}^{Pot}$ for valinomycin in diphenyl ether (25° C) (Preference of M^+ over K^+)

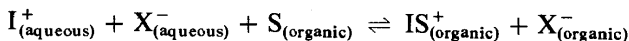
$K_{K^+M^+}^{Pot}$	M^+						
	Rb^+	K^+	Cs^+	NH_4^+	Na^+	Li^+	H^+
	1.9	1	3.8×10^{-1}	1.2×10^{-2}	2.6×10^{-4}	2.1×10^{-4}	5.6×10^{-5}

sensors (Figure 5) having a theoretical linear electrode function (EMF versus $\log a_{K^+}$) in the range 10^{-1} to $10^{-5}M$ (Figure 6) with selectivities of K^+ over Na^+ of around 4000 (Table 1) and electrode resistances of about $1M\Omega$ ¹⁶. In analogy to equation 1 the EMF of such a sensor is given by (for conditions, cf. refs 9 and 2)

$$EMF(T) = E_0^D + \frac{RT}{F} \ln \left[a_{K^+} + \underbrace{\frac{u_{MS^+} K_{M^+}}{u_{KS^+} K_{K^+}} a_{M^+}}_{K_{K^+M^+}^{Pot}} \right] \quad (6)$$

* Type MF; Millipore Filter Corp., Bedford/Mass. USA.

where a_{M^+} is the activity of the interfering ion, u_{MS^+} , u_{KS^+} are mobilities of electrically charged complexes within the membrane, and K_{K^+} , K_{M^+} are equilibrium constants of the following salt extraction



Since in most cases $u_{MS^+} \approx u_{KS^+}$, the selectivity constants of liquid membrane sensors with electrically neutral ligands are mainly given by the ratios of the equilibrium constants K^+ and M^+ which are determined in part by the complex formation constants of the antibiotics and also depend on the other components of the membrane.

Table 2. Selectivity constants $K_{NH_4^+ M^+}^{Pot}$ for a saturated solution of nonactin (72%)–monactin (28%) in tris(2-ethylhexyl) phosphate. (Preference of M^+ over NH_4^+)

	M^+						
$K_{NH_4^+ M^+}^{Pot}$	Li^+	Na^+	K^+	Rb^+	Cs^+	Ca^{2+}	H^+
	4.2×10^{-3}	2.0×10^{-3}	1.2×10^{-1}	4.3×10^{-2}	4.8×10^{-3}	1.7×10^{-4}	1.6×10^{-2}

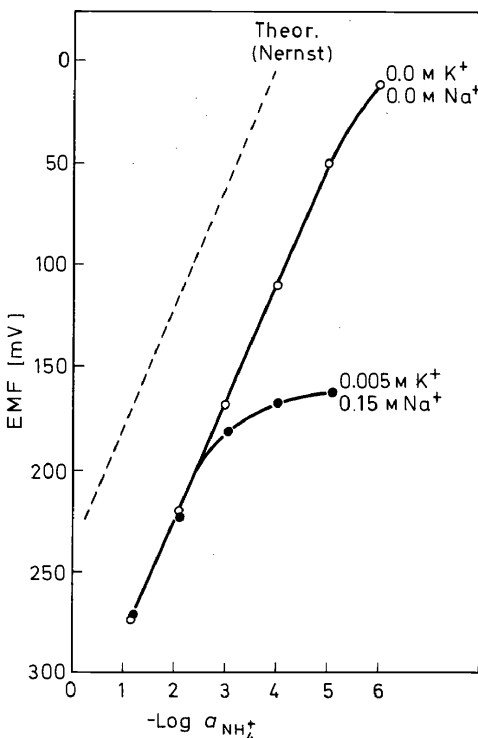


Figure 7. Electrode function of a liquid membrane sensor using nonactin (70%) and monactin (28%) in tris(2-ethylhexyl) phosphate¹⁹.

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Prodigiosin

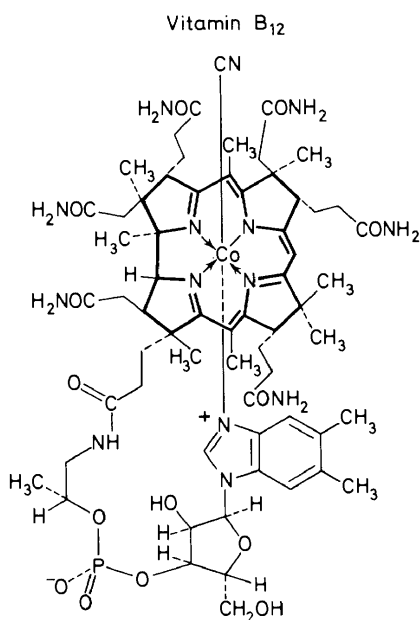
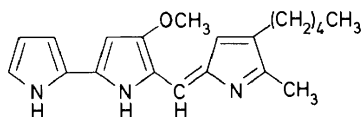


Figure 8. Structures of prodigiosin²² and vitamin B₁₂.

Since antibiotics exhibiting a decided preference for complexation with NH_4^+ over alkali ions exist, liquid membrane sensors for the selective detection of NH_4^+ have become possible (Figure 7, Table 2)¹⁹. Sensors using valinomycin as membrane component have been successfully applied in the determination of K^+ in undiluted blood serum using one minute readings²⁰. The reproducibility of a single determination is 0.07 mequiv./ K^+ (standard deviation)²⁰. Work is in progress to utilize the NH_4^+ liquid membrane sensor in measuring blood urea by treating blood serum with urease²¹.

Undoubtedly, mixed salt solid-state membrane electrodes offer a host of attractive applications in the field of selective ion detection, yet the potential of liquid membrane electrodes is virtually unlimited. Since our knowledge of ion selectivity is at present rather meagre, finding adequate ligands becomes a problem in itself. Compounds of biological interest may, however, give some hints. For example the antibiotics prodigiosin²² and vitamin B₁₂* (Figure 8) give a response to anions in liquid membrane electrodes of the type shown in Figure 5²³ (see Figures 9 and 10).

* Fluka AG, Buchs, Switzerland.

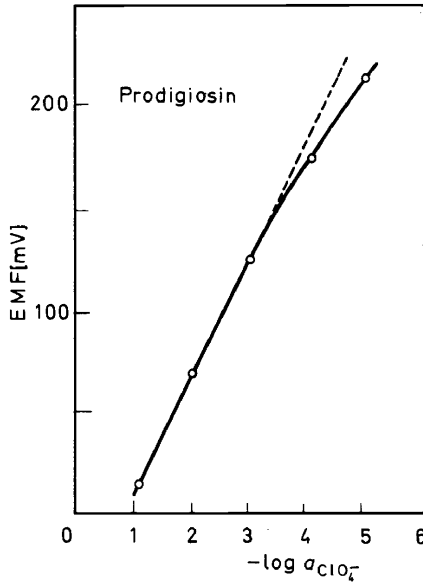


Figure 9. Electrode function of a liquid membrane sensor using prodigiosin²² in 1-decanol.

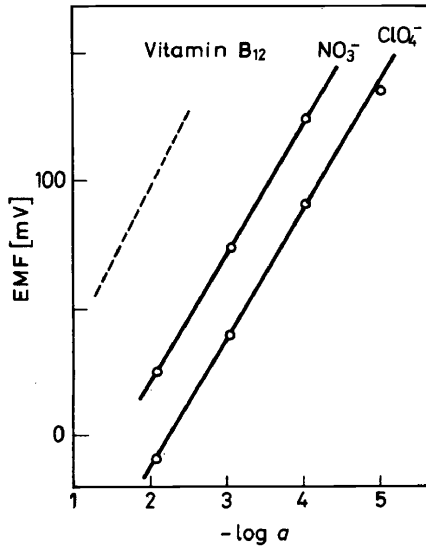


Figure 10. Electrode function of a liquid membrane sensor using vitamin B₁₂ in 1-decanol²³.

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Our knowledge of the behaviour of ion selective electrodes is enhanced by *ab initio* calculation of the energy of interaction of an ion with a ligand. The result of an attempt to calculate the free energy of interaction ΔG_{calc}^0 of different ions with water as the ligand (free energy of hydration) is given in Table 3 as a function of the coordination number. To compute the interaction electrostatic contributions (charge/dipole, charge/induced dipole,

Table 3. Calculated and observed free energies of hydration and coordination numbers of some cations

Ion	ΔG_{calc}^0 (kcal/mole) for coordination number				$\Delta G_{\text{expt.}}^0$ (kcal/mole)	$n_{\text{exp.}}$
	2 linear	4 tetrah.	6 octah.	8 cubic		
Li ⁺	-94.9	-106.6	-112.3	-78.4	-114.3	
Na ⁺	-80.4	-88.2	-92.0	-84.6	-89.1	6
K ⁺	-66.1	-70.0	-71.7	-67.9	-71.7	4-6
Rb ⁺	-61.9	-65.0	-66.2	-62.6	-67.4	
Cs ⁺	-56.6	-58.5	-58.9	-55.2	-61.9	7
Be ²⁺	-468	-539	-468	-353	-565.2	4
Mg ²⁺	-373	-417	-458	-370	-436.8	6
Ca ²⁺	-312	-341	-372	-387	-347.5	
Sr ²⁺	-293	-319	-347	-366	-333.9	
Ba ²⁺	-266	-287	-310	-327	-307.0	
Ra ²⁺	-258	-279	-303	-320	-306	
Zn ²⁺	-368	-415	-457	-392	-466.1	
Cd ²⁺	-324	-361	-396	-407	-410.7	
Sn ²⁺	-334	-375	-414	-413	-371.4	
Hg ²⁺	-305	-339	-373	-396	-426.8	
Pb ²⁺	-290	-320	-352	-373	-339.5	
Ti ²⁺	-324	-358	-393	-394	-426	
V ²⁺	-336	-374	-411	-394	-441	
Cr ²⁺	-334	-371	-407	-393	-444.8	
Mn ²⁺	-354	-397	-437	-393	-420.7	
Fe ²⁺	-368	-415	-457	-393	-443.2	
Co ²⁺	-373	-421	-465	-393	-460.6	6
Ni ²⁺	-380	-431	-476	-392	-478.4	4-6
Cu ²⁺	-373	-421	-464	-392	-482.2	
Al ³⁺	-889	-983	-1023	-783	-1078	6
Sc ³⁺	-748	-811	-884	-813	-900	
Ga ³⁺	-855	-950	-1043	-824	-1078	6
Y ³⁺	-707	-763	-829	-826	-826	
La ³⁺	-636	-679	-734	-778	-766	9
Cr ³⁺	-850	-945	-1039	-826	-1037	6-7
Fe ³⁺	-846	-941	-1036	-829	-1033	
Co ³⁺	-850	-944	-1038	-826		

dipole/dipole, dipole/induced dipole, induced dipole/induced dipole, charge/quadrupole, dipole/quadrupole, induced dipole/quadrupole, quadrupole/quadrupole) and dispersion energy terms (ion/molecule, molecule/molecule) as well as the repulsion (ion/molecule, molecule/molecule) have been included²⁴. The agreement between experimental values and the ones com-

puted for the coordination number giving the most stable hydrates is very good. Similarly the coordination numbers determined in this way agree with experimental data (Table 3). Work is in progress to extend the computation to other ligands²⁴.

Extremely high selectivities are obtained if an enzymatic degradation of the components to be determined can be used. The enzyme-carrying matrix is sandwiched between the sample solution and a sensor which detects one of the degradation products (Figure 11)²⁵.

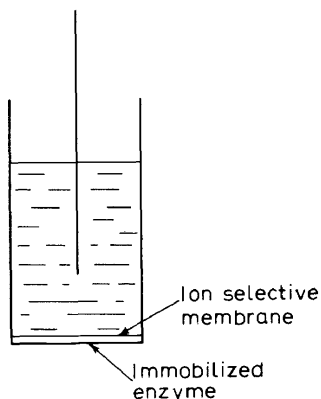


Figure 11. Schematic diagram of a membrane electrode using immobilized enzymes²⁵.

There is no doubt that as yet only a few possibilities for the production of ion selective sensors have been pointed out. There is therefore real hope that research in this area will drastically influence analytical chemistry in the widest sense^{2, 26}.

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