Devices for ion-sensing and pX measurements*

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Abstract: Thirty years of ion-selective electrode (ISE) researches at the University of Wales, Cardiff are outlined. They summarize developments of PVC membrane ISEs, first for calcium and then of other systems, including the improved calcium dioctyl-phenyl-phosphate sensor for calcium and those of ion-exchangers, polyalkoxylates, and cyclic and acyclic polyethers for various anions and cations. Electrodes based on polyalkoxylates have interesting properties toward the polyethers themselves. Some ISE failure causes are discussed. Attention is given to applications, including analysis of wash liquors and nonionic surfactants, biomedical roles, and studies of sulfate-reducing bacteria activity. Coated-wire ISEs and ion-selective field effect transistors (ISFETs) are mentioned, as are other modes of ISE deployment. The review concludes with some fundamental features of PVC electrode membranes as determined by radiotracer, applied potential, and potentiostatic approaches.

INTRODUCTION

Discovery of the glass electrode for hydrogen ions by Cremer in 1906 stimulated the making of chemical measurements with physicochemical instrumentation. This has evolved by advances in electronics, instrumental control and data processing, and in sensors and detectors—particularly by the massive research efforts of the second half of the 20th century. Sensors for pH and pX are based on glass, crystal, and PVC matrix membranes [1], with significant legacies by ion-selective electrodes (ISEs). Of special import are ISE-based measurements of blood electrolytes, which have replaced flame spectrometric methods. Progress in the field has been described in (*Ion-*) *Selective Electrode Reviews* over 1979 to 1992 [2] and other reviews [3,4].

In celebrating "One Century of pH and pX Measurements", it is a privilege to outline our ISE researches done in the Redwood Building of the University of Wales, Cardiff. Characteristics of existing ISEs [5,6] and selectivity ratings [6–8] were first studied. But of high priority was the need for improved exploitation in ISEs of selective liquid ion-exchangers which led to creation of the PVC matrix ISE membranes [9,10], made by adding liquid ion-sensor to a solution of PVC in tetrahydrofuran set in a glass ring on a glass plate, and allowing the tetrahydrofuran to evaporate to leave a master membrane for assembly of ISEs [9,10]. The first such PVC ISE was a trapped organophosphate liquid calcium ion-exchanger system for pCa measurements [9], to be followed by others for nitrate [11] and potassium [12], the latter of which extended the principle to a coated-wire electrode—a form also of independent creation [13].

The PVC principle for making ISE membranes attracted much attention and was adopted by the Zürich school for ISEs based on valinomycin and other neutral carrier sensors [14,15]. Indeed, the PVC matrix concept was the essential breakthrough that led to the almost universal clinical use of ISEs [16] for determining blood electrolytes [17], and for other applications [18].

As at places elsewhere, studies at Cardiff involved optimum membrane compositions [19], alternatives to PVC [20–24], and solvent mediators [25–28]—with tripentyl phosphate being an alternative

to dioctylphenylphosphonate (DOPP) in dialkylphenyl-phosphate based calcium ISEs [29,30]. These elucidated aspects of calcium electrode selectivity [30–32].

RESEARCHES ON CALCIUM ISES

Improvements in sensors have been rewarding, such as replacing calcium didecylphosphate by calcium bis-di-(1,1,3,3-tetramethylbutyl)-phenyl-phosphate [33], which itself is synthetically more accessible than its equally suitable n-octyl isomer [34]. These calcium sensors are useful alternatives to ETH 1001 neutral carrier [33]. Nitrated modes of dioctyl-phenylphosphate sensors and phosphonate mediators offer little gain in calcium ion-sensing and not much for other ionic species [26,35–37]. Also, attempts to extend electrode lifetimes by grafting sensors and/or plasticizing solvent mediators on to the polymer matrix offered little reward [38–40].

Apart from biomedical roles [40–42], calcium ISEs can be used to monitor pCa in detergent wash liquors. Hence, much effort at Cardiff went on overcoming interferences by surfactant anions [43–45], and in adapting the systems of the above researches for exploring prospects for pCa measurements in wash-type liquors [43–45]. This entailed long-range calibrations with ion-buffers [33,46,47], i.e., to pCa ~8, and determinations of stability constants [48,49]. Electrodes were calibrated in the dip-type (static and the superior dynamic mode in respect of response times [50]), flow-injection and flow-through modes [46]. Trioctyl phosphate solvent mediator gave improved resistance to interference by anionic surfactants [44,49].

Interferences of calcium ISEs extend to biomedical roles, and studies of lipid biochemicals showed cholic acid, cholesterol, lecithin, and vitamin D_2 to interfere [51]. Again, calcium ISE membranes based on trioctyl phosphate solvent mediator tended to resist interference [51]. The study was linked to sodium and potassium ISE studies on blood and urine [52]. Close to this are chemometric type model studies on multiple channel analysis of free magnesium, calcium, sodium, and potassium at physiological concentration levels [53,54].

APPLICATIONS AND ERROR CAUSES

These include carboxylate interferences of the lanthanum ISE [55] and chloride interference films of copper(II) ISEs [56,57]. Much effort was put into recognizing potential errors in chloride (and sodium) ISEs used for sweat screening in diagnosing cystic fibrosis in infants [58–60]. Examinations have also been made of electrode surfaces, namely microscopy [19] and X-ray fluorescence study of interferences by surfactants on PVC calcium ISE membranes [45], X-ray fluorescence, scanning electron microscopy (SEM), and ESCA examination of PVC membranes containing barium-polyalkoxylate complexes [61], and SEM of silver sulfide ISE surfaces [62].

Of much importance was confirmation that sulfide [63] and iodide [64] ISEs had longer working ranges than implied by a silver defect theory. Hence, sulfide ISEs can measure pS to >12 in sulfate-reducing bacteria cultures [65,66], and the electrode has been used for studying the metabolism of various sulfate-reducing bacteria [67,68], and roles in metallic corrosion [66–69]. Continued studies showed a prospective role for sulfide ISEs to monitoring thiols [70], and the ISE has been assessed for pS determinations in environmental monitoring [71].

Studies of ISEs, applied for pX measurements, extend to vegetables, fruits, juices and oils [72], coffee and tea [73], and skim milk powder [74].

POLYALKOXYLATE SYSTEMS

An important aim of scientific research and development is the search for improved methods and new tools. Hence, the focus on new sensors among tetraphenylborates (TPBs) of barium adducts of nonylphenoxypoly(ethyleneoxy)ethanols (NPs). These trade as Antarox and Igepal nonionic surfac-

tants, and a PVC ISE based on the member of 30 ethyleneoxy units (CO 880), with 2-nitrophenyl phenyl ether as plasticizing solvent mediator, is creditable for barium [75].

On fundamental aspects, data of solvent extractions into dichloromethane of NP picrates match trends in selectivity of NP-TPB ISEs [76]. Infrared and NMR spectroscopy of NP-TPBs indicate an ethoxylate:cation ratio of 12:1 for alkaline earth complexes and 8.5:1 for sodium complexes, while the ratios for ordinary polyethylene glycol are ~10.5:1 [77].

Unusual in the matter of pX measurements is the response of the NP-based barium ISE to alkoxylates, with the emf of the ISE increasing by 100 mV for added NP (Antarox CO-880) in the 2×10^{-5} to 10^{-3} M range, i.e., linearly with log [alkoxylate] [78]. The feature applies to various NPs, i.e., Antarox CO-430, -630, -730, -850, 880 and -890; to the octyl (OP) counterparts, i.e., CA-120 and Triton X-100, and others of the nonionic variety, including Dobanol 25-7, Lutensol A07 Synperonic 7, polyethylene glycol (PEG 1025), and poly(propylene glycol) (PPG 1025) [78]. An added feature is a break in linearity attributed to critical micelle concentrations (CMCs) of the respective nonionic surfactants [78].

Barium complexes of other polyalkoxylates, set up as PVC electrodes, respond similarly to barium and toward the nonionic surfactants, but in a manner inferior to Antarox CO-880 toward barium [79]. It was the electrode based on Antarox CO-430 that excelled toward the surfactants, and the system for determining Dobanol 25-7, Synperonic 7, and Lutensol A07 in detergent powders yielded good recoveries [79].

Interferences of polypropoxylate-based ISEs indicated the prospect of an ISE for lithium [80], with DOPP or dioctyl-3-nitrophenylphosphonate as solvent mediator. However, rather than the lithium adduct, a barium adduct, Ba(PPG 1025)$_{0.69}$. TPB with DOPP, proved to be better, as assessed in a microconduit flow injection analysis system [81]. But, this did not excel over systems based on alternative sensors of cyclic molecules, i.e., dodecylmethyl-14-crown-4(6-dodecyl-6-methyl-1,4,8,11-tetraoxacyclotetradecane) and N,N.N',N'-tetraisobutyl-cyclo-hexane-*cis*-1,2,-dicarboxylic diamine [81]. However, put to the test on ten samples of blood serum containing between 0.21 and 2.00 mM of lithium, it was necessary (for data to match those of flame photometry) to carry out the lithium ISE measurements by first adjusting the serum sodium chloride level to 153.9 mM [82]. The Ba(PPG 1025) electrode proved to be the best; but even so, it was for just five samples that good results were obtained.

Before leaving the alkoxylates, it is noted that of polyethylene glycol (PEG 1540), Antarox CO-880, and polypropylene glycol 425 (PEG 425), the last two have lead(II) ISE features for alkoxylate TPBs with 2-nitrophenyl phenyl ether in electrode membranes [83].

CYCLIC AND ACYCLIC NEUTRAL CARRIER SYSTEMS

First studies on ISEs for diquat (DQT) and paraquat (PQT) herbicides were on dibenzo-30-crown-10 (DBC10) crown ether [84]. Selectivities for the herbicides over other cations improved significantly when ion-pairs with TPB were set in the membrane compositions with 2-nitrophenyl phenyl ether as mediator [84]. It also transpired that PVC membranes of PQT-TPB with either 2-nitrophenyl phenyl ether or 2-nitrophenyl octyl ether functioned as paraquat ISEs [84]. In a study of more ion-pairing agents, phosphorus hexafluoride, TPB, and tetra-kis-4-chlorophenylborate (T4ClPB) gave good electrodes, but the first named was not selective [85]. ISEs with T4ClPB were the best with good response for diquat (3×10^{-8} M) or paraquat (2×10^{-7} M) [85]. Selectivity coefficients for these ISEs are near to those calculated, while those for 4,4'-dipyridium (4,4'-DPy) as model systems showed an anomalously poor selectivity [85].

A wider search for ISEs of 4,4'-DPy, DQT, and PQT involved various conformational crown ethers [85], but it was only for 4,4'-DPy that viable ISEs were obtained. Calibration slopes ranged between 33 and 41 mV decade^{-1}, extending down to 1.7–6 µM, with low interferences from potassium, ammonium, guanidinium, barium, diquat, and paraquat [86].

The crown ethers assessed for DQT and PQT can, with a suitable solvent mediator, yield ISEs for other species. Hence, a guanidinium ISE system of dibenzo-27-crown-9 (DB27C9) with guanidinium

TPB and dibutyl phthalate as solvent mediator [87]. This system is excelled by a similar one involving bis(metalphenylene)-26-crown-8 (BMP26C8) with either dibutyl phthalate or dioctyl adipate as solvent mediator [88].

Disubstituted diphenyl ethers of tetraethylene glycol [89], and bis(crown ethers) [90] have promise as sensors for alkali and alkaline earth cations. Most promising are bis(crown ethers), with bis[(12-crown-4)-2-ylmethyl]-2-dodecyl-2-methyl malonate simulating sodium glass electrodes, and bis[(benzo-15-crown-5)-15-ylmethyl] pimelate being similar to valinomycin for potassium [90], each with 2-nitrophenyl phenyl ether as solvent mediator and potassium T4ClPB as anion excluder. However, data for sodium and potassium measurements in blood serum had shortcomings in correlations with flame photometric measurements [90].

Macrotetrolide antibiotics were early candidates as ISE sensors. Monensin, salinomycin, nonactin, and narasin, have been reexamined [91] as ammonium sensors. Nonactin, with dioctyl adipate as solvent mediator was best, followed by salinomycin. As the aim was to assess prospects for ammonium-sensing in respect to enzyme-based sensors for urea. This was achieved by using complementary membranes of entrapped urease [92]. A study of solvent mediator effects on the nonactin ammonium ISE, used also in the flow injection analysis mode, focused on 2-nitrophenyl octyl ether and trioctyl phosphate, which had advantages over dioctyl adipate [93].

In anticipation of new and improved systems, exploration for sensors never ceases. An interesting prospect lay with representatives of planar and tripodal "scorpion-like" ligands, each with oligoether "tails" and a pair of anionic pincers. Their affinity for barium led to testing as barium ion-sensors [94], but performance was inferior to polyalkoxylate-based barium ISEs [75]. Thus, there was fortuity in early discoveries of ISEs, also exemplified by another study [95] showing a system of 4'-picrylamino-5'-nitrobenzo-18-crown-6 to have good selectivity for potassium, but falling short of its valinomycin precursor.

ISFTET STUDIES

Solid-state ISEs have inherent advantages by obviating the use of internal reference solutions; hence, researches on liquid ion-sensors in the early 1970s took on coated-wire versions of PVC electrodes [96]. Attention continues, and they lend themselves nicely to pX determinations in microconduit flow modes, used for some of the studies surveyed here [81,82].

Ion-selective field effect transistors (ISFETs) have yet to achieve their potential, but their study has led to modifications in membrane design and photocuring encapsulation [23,24,97] and to features concerning gate dimensions and ion-implantation levels [98]. On membrane matrices, incorporating copolymer of PVC with poly(vinyl alcohol) and silicon tetrachloride in the PVC membrane composition increases membrane adhesion to the gate [97].

FUNDAMENTAL ASPECTS

Relations between alkoxylate-based ISEs and solvent extraction of picrates [76,77] extend to other correlations between solvent extraction parameters and ISE function for cations, and also toward alkoxylates [99]. There is also an analogy between diquat, paraquat, and 4,4'-dipyridinium ISE function and ion-pair extraction into an organic phase [85].

Radiotracer studies have yielded helpful information. Those on polyalkoxylate interaction with PVC electrode membranes containing barium-polyalkylate complexes show Antarox CO-880 to be absorbed by membranes containing other alkoxylate nonionic surfactants, i.e., due to barium ions within the membranes favoring the Antarox CO-880 [61]. Polyalkoxylate membranes do not permeate ions to any significant extent [100].

Ion-permeation studies with radiotracers were productive for organophosphate PVC matrix membranes, indicating selective permeation of calcium ions over other alkaline earths, etc. [101,102].

Radiotracer permeation from active to inactive solutions showed PVC membranes to yield better calci-um ion permeation than polyacrylate types [103]. Also, neutral carrier type membranes were much less permeable to radiotracer ions than liquid ion-exchanger (organophosphate) types [103]. However, per-meability was enhanced somewhat for neutral carrier membranes based on 2-nitrophenyl phenyl ether, particularly if potassium T4ClPB anion excluder was also present [103].

There were prominent differences between PVC membranes of liquid ion-exchanger and polyalkoxylate neutral carrier types under conditions of applied potential [104]. Thus, PVC membranes containing organophosphate liquid ion-exchanger, under conditions of applied potential, maintained stable current flows over prolonged periods unaffected by polarity reversals, i.e., 5 to 6 μA current for 2V applied potential. However, current fell rapidly for polyethoxylate type membranes current, and did not recover on polarity reversal of applied potential—indicating a breakdown of the cation-polyalkoxy-late structure [104].

Finally, experiments by a four-electrode potentiostatic technique on facilitated ion transfer of alkali metal ions from water to nitrobenzene containing various crown ethers indicated trends in com-plex formation [105]. Interestingly, the stabilities of sensing complexes of cations and the ionophore are of the same order of magnitude for polymer and polymer free-solutions, and the diffusion coefficients are similar when PVC is introduced into the nitrobenzene phase [105]. However, for polymethyl-methacrylate polymer, the diffusion coefficients are slightly smaller—probably because the phase pres-ents a more tortuous route [105].

CONCLUSION

This survey, at near to the centenary of the discovery of the glass electrode for hydrogen ions, illustrates the activities at one center from among many engaged on researches of pH and pX devices and meas-urements. It demonstrates the effort of searching for devices—whether they are used for producing data by direct reading, or by addition/subtraction, or by circuitous routes such as by indicator electrodes in potentiometric titrations. The researches have yielded a huge legacy of devices and methods for various scientific areas—especially in clinical medicine where they will increasingly interact on the general human population, without most realizing it!

The significance of electrochemical sensors is such that in the mid-1980s the Japanese Ministry of Education sponsored a "Database on Electrochemical Sensors" [106]. This, for data extracted from the world's scientific publications/journals over 1983 to mid-1986, sets the above program in the world's leading half-dozen.

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