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STUDIES ON POTENTIOMETRIC TITRATIONS USING SIMPLE LIQUID MEMBRANE-BASED ELECTRODES:
COATED WIRES VS. CARBON PASTES

Karel VYTŘAS[1], Jitka JEŽKOVÁ, Vilém DLABKA and Jaromír KALOUS
Department of Analytical Chemistry, University of Pardubice,
CZ-53210 Pardubice

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An overview is given on the use of simple potentiometric sensors to monitor titrations based on various principles. Earlier results obtained with polymeric membrane electrodes of the coated-wire type are compared to those taken with carbon paste electrodes. Both the types can be recommended as simple and inexpensive sensors suitable to monitor titrations based on ion-pairing principles. It is expected that an organic solvent present in both the sensors (a membrane plasticizer or pasting liquid) is saturated with an ion-pair formed within such a titration on extraction principles, thus giving selective ion-exchanging electrodes. Although in acid-base titrations and some of determinations based on both oxidation-reduction and precipitation reactions the potential breaks can also be obtained, authors prefer monitoring of them with other suitable sensors.

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[1] To whom correspondence should be addressed.

Introduction

The last quarter of this century will be always mentioned as a period connected with the rapid development of a new type of potentiometric sensor, ion-selective electrodes (ISEs). The membrane systems of these, originally formed from solid or glassy electrolytes, limited their use primarily to the determination of inorganic ions. Later, when liquid ion-exchangers, ionophores, and enzymes, bacteria and animal tissue began to be used in the electrode membranes, the applications became far more extensive [1].

With regard to the liquid-state electrodes, these include membranes made of liquid substances or with electroactive substances dissolved in a suitable nonvolatile, water-immiscible solvent, called mediator. In early designs, the organic phase of these membranes was an organic solvent, placed between the two aqueous phases in bulk or with the support of a thin, porous cellulose sheet, sintered glass, or the like. As work with these membranes proceeded, more durable polymeric supports were developed, most often poly(vinyl chloride) (PVC), which is now used almost universally for this type of electrode. An electroactive compound is dissolved in a solvent (usually tetrahydrofuran or cyclohexanone) together with the PVC and a suitable plasticizer. The solvent evaporates, leaving a plasticized PVC ion-selective membrane. Because the plasticized polymer behaves like a viscous liquid, the properties of the electrode are very similar to those of the original wet membrane [2,3].

In contrast to direct potentiometric measurements requiring careful calibrations of measuring cells, the potentiometric titration techniques offers the advantage of high accuracy and precision, although at the cost of increased time and increased consumption of reagents used as titrants. A further advantage is that the potential break at the titration end-point must be well defined, but the slope of the sensing electrode response need be neither reproducible nor Nernstian, and the actual potential values are of secondary interest. This allows the use of sensors of more simplified construction.

Coated-Wire Electrodes

The first group of the simplified sensors mentioned above covers those of so-called coated-wire construction type (coated-wire electrode, CWE) introduced by Cattrall, Freiser et al. [4-6]. As shown in numerous review papers [7-10], these devices have become attractive because of the ease with which they can be fabricated and manipulated. Although different materials can serve as central conductors, an extensive study dealing with their application in ion-pair formation-based titration [11] has shown that when the wire support did not react with the membrane components, it had no substantial influence on the shape of the potentiometric titration curve. Because all the materials studied had to be isolated by means of glass or plastic tubes before they could be covered with a membrane, we decided to use an ordinary aluminium conductor with thick PVC insulation, which eliminates mounting the wire in a proper tube. Such sensors are really very inexpensive and may easily be constructed even from waste materials [12]. The preparation of simple coated-wire type elements has been described, and instructions for their use have been given in detail [13]. Usually we used the membrane composition obtained from a solution of PVC (0.09 g) and a plasticizer (0.2 ml) in tetrahydrofuran (3 ml). No electroactive substances were added.

Carbon Paste Electrodes

Carbon paste electrodes (CPEs) may represent the second kind of simple potentiometric sensors. Originally, they were introduced into electroanalytical chemistry in an effort to obtain an electrode with properties similar to those of the traditional mercury dropping electrode [14,15] which has, as well known, some limitation in the use in areas of more positive potentials, caused by anodic dissolution of mercury. Although the original idea to obtain similar dropping electrode consisting of a carbon paste has not been successful, the CPEs have recently found their application in numerous methods of stripping voltammetry (see reviews [16-20], the more recent references being given in another paper of this issue [21]). With regard to potentiometry, Mesaric and Dahmen [22] were probably the first to use electrodes filled with carbon paste; the paste mixtures based on carbon powder with either Nujol or parafin wax and containing a precipitated silver halide - silver sulfide exhibited a nearly Nernstian response for both halide and silver ions.

It should be mentioned that qualitatively new CPEs have been obtained by mixing carbon powder with more polar liquids used as plasticizers in PVC membrane-based ISEs [23]. For potentiometric applications, the CPEs containing nitro compounds can also be used. For example, four types of CPEs based on nitrobenzene solutions of different ion-exchangers were reported recently as ion-selective sensors for perchlorate and fluoroborate [24]. When compared with ISEs (including CWEs) based on polymeric membranes, the CPEs have an advantage of much lower ohmic resistance. The preparation of these sensors is not complicated [24,25]; the paste is obtained by thorough mixing of 1.0 g of graphite powder and 0.4 ml of pasting liquid, and packed into a piston-like electrode body with a conductive contact.

Titrations Based on Ion-Pair Formation

As mentioned above, no electroactive substances were added during preparation of CWEs. Before application they were conditioned, either by dipping the membrane into a stirred aqueous suspension of the determinand-titrant ion-pair or directly, within the first ion-pair formation-based titration [11,13]. With regard to CPEs, the composition of carbon pastes makes possible to classify them as ion-selective liquid membrane type electrodes; pasting liquids exhibit usually good extraction ability against ion-associates composed of lipophilic species. This is why they could also be applied to monitor titrations based on ion-pair formation [24,26-28] after similar conditioning.

In precipitation titrations, it is well known that the magnitude of the potential break is governed predominantly by the solubility product of the precipitate formed. However, when the precipitate is extractable into the membrane mediator, the role of the extraction parameters must also be taken into account. A quantitative expression for the precipitation equilibrium is given by the solubility product, $K_s(QX)$, which is defined by

$$K_s(QX) = [Q^+][X^-] \tag{1}$$

In the presence of another, immiscible organic solvent, another equilibrium is attained because the two ions will form an associated ion-pair in a phase of lower polarity,

$$Q^+_{aq} + X^-_{aq} \rightleftharpoons QX_{org} \tag{2}$$

characterized by the extraction constant, $K_{ex}(QX)$,

$$K_{ex}(QX) = [QX]_{org}[Q^+]^{-1}_{aq}[X^-]^{-1}_{aq} \tag{3}$$

The distribution ratio of Q^+ ion, $D(Q^+)$, can be expressed by

$$D(Q^+) = [QX]_{org}[Q^+]^{-1}_{aq} = K_{ex}(QX)[X^-]_{aq} \tag{4}$$

It is expected that during conditioning, an organic solvent (a plasticizer in CWEs or pasting liquid in CPEs) becomes gradually saturated with the ion-pair QX. In the absence of side reactions, the ion-pair concentration in the organic phase which is in contact with an aqueous suspension of the same ion-pair is determined by the two above constants,

$$[QX]_{org} = K_{ex}(QX) \cdot K_s(QX) \tag{5}$$

This concentration can be considered as that of ion-exchanging sites in the membrane of such a Q^+ (or X^-) selective electrode. It follows that this concentration increases with increasing values of both the extraction constant and the solubility product of the ion-pair formed [29]. When the titration system (titrant, determinand, or both) is changed, usually two titrations are needed to recombine the ion-pair in the organic phase for the new one [9,11]. The role of extraction parameters in measurements with liquid and/or plastic

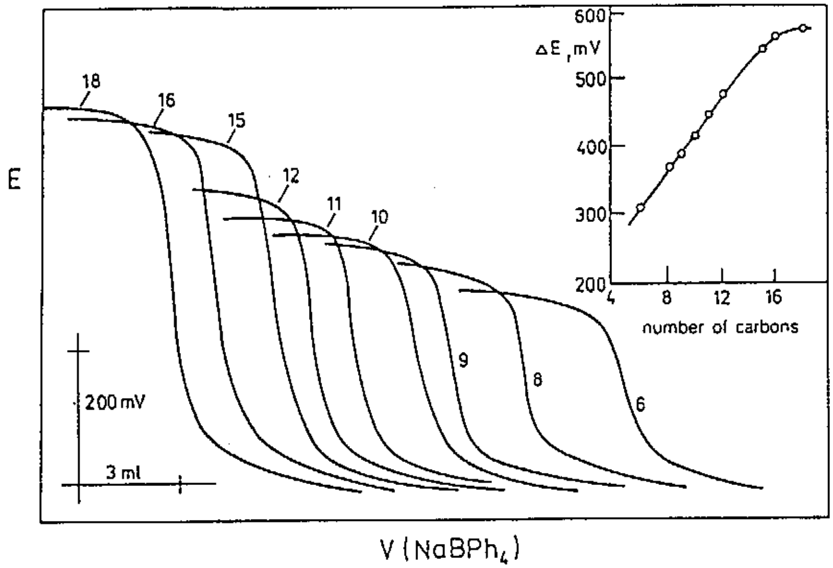

Fig. 1 Potentiometric titration curves for N-alkyl-N-ethylpyrrolidinium salts titrated with 0.01 M sodium tetraphenylborate. Measured with a cell consisting of a coated-wire electrode (Al | PVC + 2,4-dinitrophenyl *n*-octyl ether) and a double-junction calomel electrode. The numbers next to the titration curve give the numbers of carbon atoms in the alkyl chain. Top right: Dependence of the potential break magnitude on the alkyl-chain-length. From Ref. [1] with permission

membrane-based ISEs was studied by numerous authors [29-36] and is mentioned also in another paper of this issue [37].

In titrations of organic cations, the solubility of the corresponding ion-pair decreases and consequently, both the steepness and the overall change of the potentiometric cell voltage increase with increasing mass of the cation [38]. For example, these influences were demonstrated in the titrations of the cations of homologous series of tetraalkylammonium salts [39].

When cations of the homologous series of N-alkyl-N-ethylpyrrolidinium salts were titrated using sodium tetraphenylborate (Fig. 1) and monitored with CWEs containing various plasticizers, the values of both the distribution ratios and the extraction constants as well as the solubility products of N-alkyl-N-ethylpyrrolidinium tetraphenylborates were determined to explain the role of the equilibria involved [29]; the values of the potential break could readily be correlated with the logarithmic values of the extraction parameters (Fig. 2). Having used a CPE containing tricresyl phosphate as pasting liquid in titrations of homologous series of other quaternary salts, analogous dependences as described for CWEs have been obtained [40]; an example is shown in Figs 3 and 4.

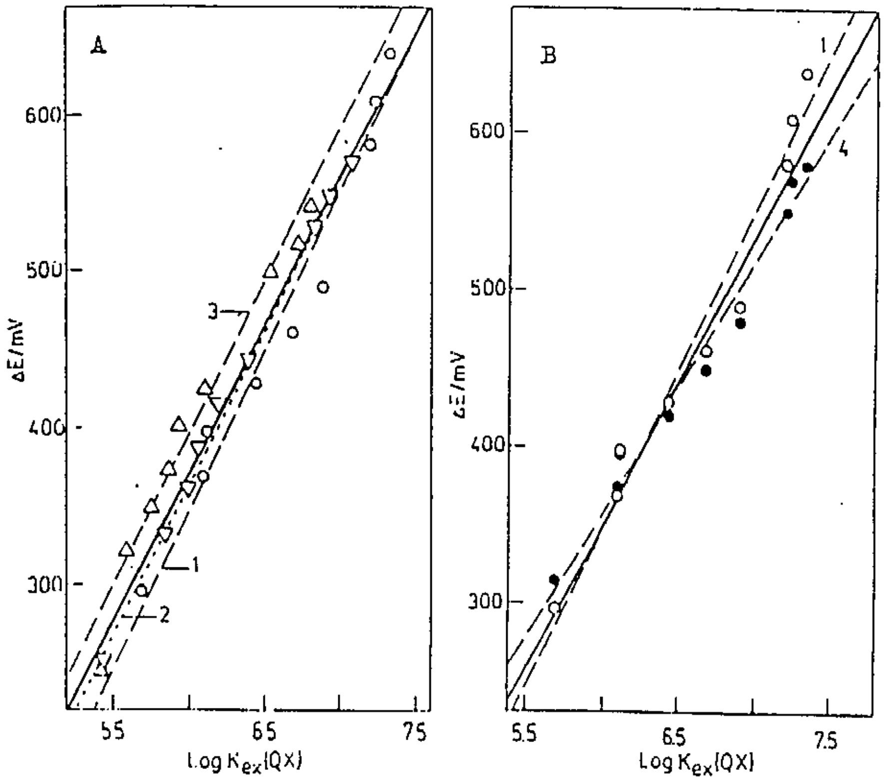

Fig. 2 Relationship between the magnitude of the potential break and the logarithm of the extraction constant of N-alkyl-N-ethylpyrrolidinium tetraphenylborates. Left (A): Titrations monitored using coated glass electrodes; PVC membrane plasticized with (1) 2,4-dinitrophenyl *n*-octyl ether (DNPOE), (2) dibutyl phthalate, (3) bis(2-ethylhexyl) phthalate. The full line is the regression line for all the plasticizers. Right (B): Titrations monitored using DNPOE-plasticized membrane electrodes. Support and the titration mode: (1) glass, manual titrations, (2) aluminium, automatic titrations. The full line is the regression line for both the electrodes. From Ref. [29] with permission.

Are these CWEs and CPEs Universal Titration Sensors?

The headline of this paragraph is not quite adequate as it may be written for all construction types of ISEs with liquid membranes. It is evident from the viewpoint of the rules for the composition of ion-pairs incorporated in the membranes and their extraction ability that mostly each of such ISEs can be used to monitor the titrations accompanied by ion-pair formation.

Numerous papers, however, deal with applications of liquid membrane ISEs in titrations based on other principles. So, for example, nitrobenzene extract of the ion-pair composed of benzyldimethyltetradecylammonium and

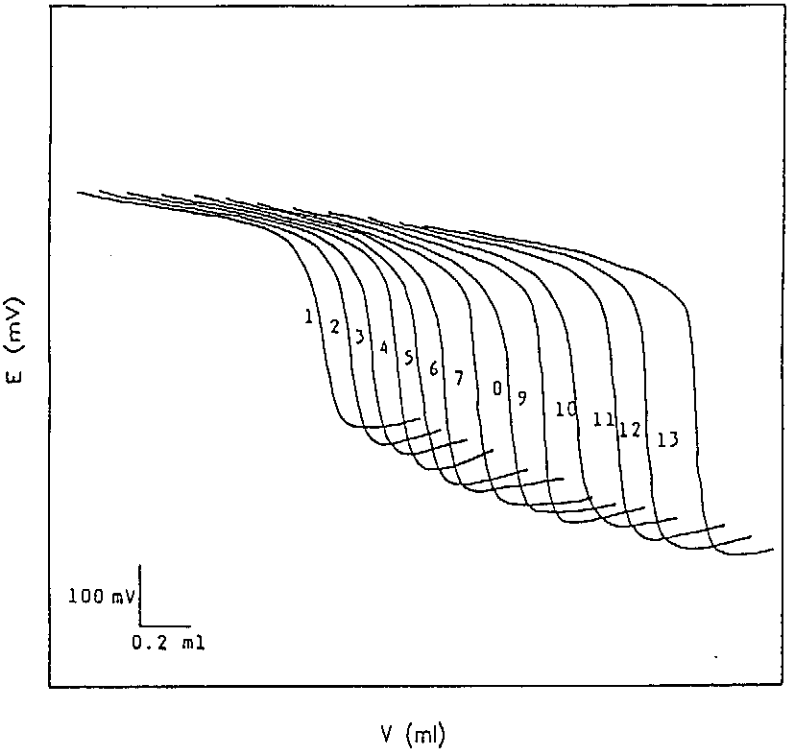

Fig. 3 Automated potentiometric titrations of quaternary salts of the $[CH_3(CH_2)_{10}CH_2CH_2N(CH_3)_2R]^+Br^-$ type. Taken ca. 0.01 mmol of the corresponding salt, titrated with ca. 0.01 M sodium tetraphenylborate. Numbering of the curves corresponds to the number of carbon atoms in N-alkyl chain (R). Monitored using a cell consisting of a CPE containing tricresyl phosphate and a double-junction calomel electrode. From Ref. [26] with permission

pyrocatechol violet has been employed as an ion-exchanger for the electrode, exhibiting nearly Nernstian response to this anionic sulfonephthalein dye, but the electrode found its main utilization in monitoring EDTA titrations of copper(II), iron(III) and cobalt(II) ions [41]. Similar ISEs containing ion-pairs of either ethyl violet with pyrocatechol violet [42] or benzyldimethyltetradecylammonium with Chromazurol S [43] have been applied in chelatometric determinations of various metal ions. An ion-pair of Rhodamine B with bis(2-ethylhexyl) sulfosuccinate in nitrobenzene has been used as an liquid membrane of a sensor indicating iodometric titrations [44], an ISE with nitrobenzene extract of benzyldimethylhexadecylammonium permanganate has been used in titrations with permanganate [45].

Christian and Stucky [46] were probably the first to mention such behaviour of liquid membrane-based ISEs; their PVC membrane softened with diphenyl phthalate and containing dithizone as a chelate-forming agent could

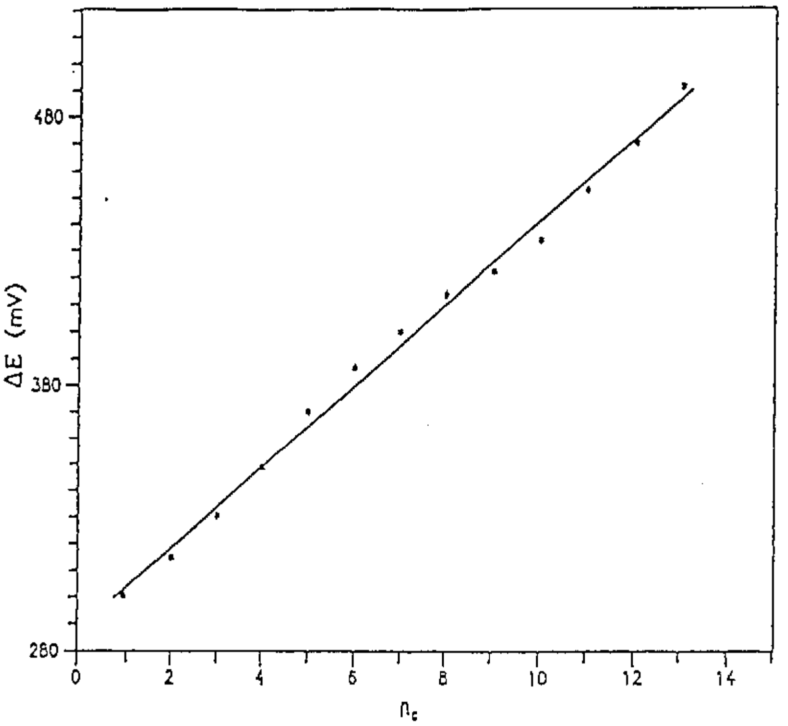

Fig. 4 Relationship between the potential break magnitude and the number of carbon atoms in the alkyl chain. Experimental data as under Fig. 3. From Ref. [26] with permission.

serve as a Pb^{2+}-ISE with a response of 27-28 mV per decade and, as expected, could also be used to monitor precipitation titrations of lead(II) with phosphate, tungstate, chromate, sulfate, oxalate and hexacyanoferrate(III). Titrations of (or with) silver(I) salts could also be monitored, which could be ascribed to limited selectivity of the above ISE (dithizone forms extractable neutral chelates with numerous heavy metal cations). The same electrode could be used in titrations of potassium(I), ammonium, thallium(I), silver(I) and mercury (II) with sodium tetraphenylborate titrant; this is also not surprising taking into account the lipophilic character of tetraphenylborate. However, potentiometric titration curves were obtained also in titrations of iron(III) with permanganate or dichromate, arsenite with iodine, copper(II), nickel(II) and mercury(II) with EDTA, or in acid-base titrations in both aqueous and acetic acid media. Thus, the authors claimed their ISE as an unique potentiometric sensor for all kinds of titrations [46]. Similarly Selig [47], partially inspired also by our papers on CWEs, prepared a simple sensor by coating a spectral carbon rod with the polymeric membrane (from a tetrahydrofurane solution of PVC and dioctyl phthalate), and appreciated it as a sensor useful to monitor ion-pair formation-based titrations as well as various other titrimetric determinations based on acid-base, oxidation-reduction or complex formation reactions.

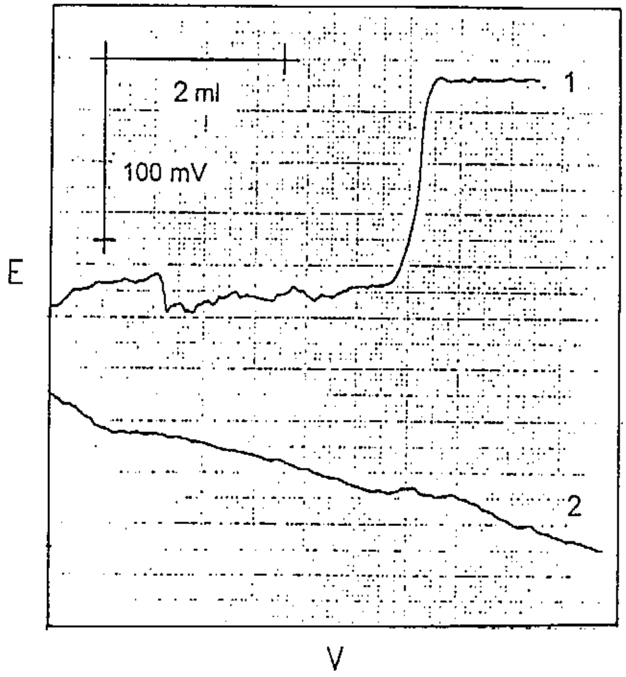

Fig. 5 Potentiometric titration of barium hydroxide (ca. 0.025 mmol) with ca. 0.01 M hydrochloric acid, monitored using a CWE (PVC + DNPOE membrane formed from their tetrahydrofurane solution and coated on aluminium support) as an indicator sensor. (1) Titration in the absence of a surfactant; (B) titration in the presence of Ajatin (benzyldimethyldodecylammonium bromide)

There are numerous explanations for such electrode behaviour, the way of sensor fabrication could be one of the cause. Most frequently, polymeric materials (especially PVC) are dissolved in tetrahydrofuran. However, hardly anybody uses the solvent of really pure quality. Marketed preparations contain, besides of declared impurities (as aldehydes, water, hydrogen peroxide), also inhibitors such as hydroquinone [48] or 2,6-di-*tert*-butyl-*p*-cresol [49]; this could cause both pH and redox interferences. Plasticizers alone can also behave as ionophores showing a Nernstian response to some ionic compounds [50].

Acid-Base Titrations

Within our earlier extensive study [51], various CWEs were prepared using different polymeric materials and plasticizers. To compare the results, also polymeric membrane-based ISEs with inner electrolyte were fabricated and commercial ISEs with polymeric membranes were used. In acid-base titrations, almost all of these electrodes gave potential break the magnitude of which was

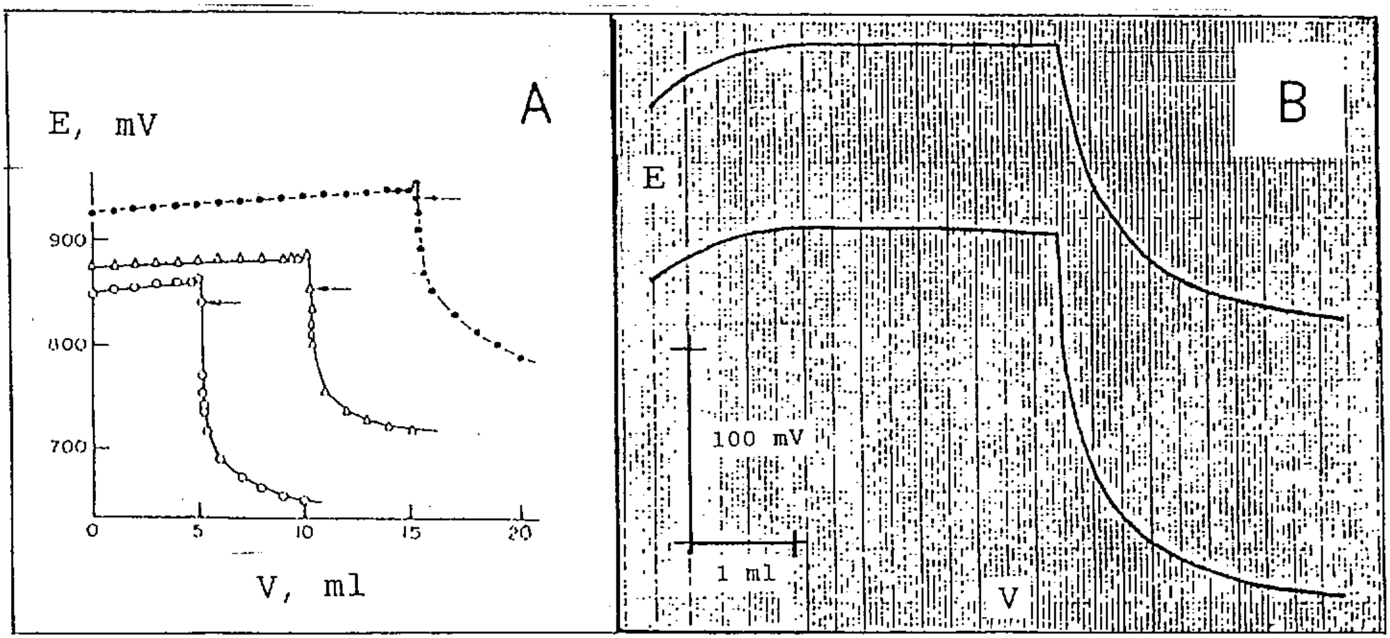

Fig. 6 Potentiometric titration of iron(II) salt with 0.002 M potassium permanganate. Left (A): Taken 0.05, 0.10 and 0.15 mmol of $FeSO_4$; manual titration monitored using a permanganate-selective electrode; a nitrobenzene extract of benzyldimethylhexadecylammonium permanganate served as a liquid membrane of the ISE and 0.01 M $KMnO_4$ as its internal electrolyte. Right (B): Taken 0.05 mmol of $Fe(NH_4)_2(SO_4)_2$; automated titration monitored using a CWE prepared by coating the aluminium conductor from a solution of PVC and DNPOE in methyl ethyl ketone. According to Refs [45] (A) and [51] (B) with permission

approximately one quarter of the corresponding break taken for the same titration using glass pH electrode. Such breaks could not be ascribed to the presence of stabilizers in tetrahydrofuran because also other solvents were used for sensors fabrication. Similarly, the choice of the matrix did not influence significantly the break magnitude; the role of PVC is probably not so important as sometimes suggested [52]. It seems more probable that these potential changes are caused by plasticizers which can have a behaviour of ionophores against hydrogen ions [50]. In addition, coulombic forces between ions and polar areas of high-molecular skeleton can occur inside of a membrane film. This can play a positive role in adsorption equilibria and foster the formation of the fixed charge on a polymer [53,54]. These influences have not been sufficiently explained until now but seem to be real; the statement is based on the fact that after addition of a surfactant (when either anionic or cationic surfactant was added to the barium hydroxide solution titrated with hydrochloric acid), the resulting potential break was significantly or completely suppressed (Fig. 5). When CPEs containing protonizable pasting liquids (e.g. tricresyl phosphate) were used to monitor acid-base titrations, potentiometric titration curves of approx. the same magnitude as those obtained with CWEs could be recorded [40].

Oxidation-Reduction Titrations

With regard to the use of CWEs as indication sensor of titrations based on oxidation-reduction reactions, it was confirmed by our experiments that the number of reaction systems where titration curves with well developed potential breaks could be recorded is quite limited [51] . In titrations of iron(II), no breaks were obtained with either cerium(IV) sulfate or potassium dichromate. When potassium permanganate titrant was used, an atypical titration curve of an unsymmetric shape was recorded. It should be assumed that in this case, the titrant is partially extracted into the membrane as the same shape of titration curves was reported [45] for electrodes containing benzyldimethylhexadecyl ammonium permanganate (to compare the records, see Fig. 6).

On the contrary, however, the shape of the titration curve taken with the use of a CPE was quite different and, in addition, titrimetric determinations of iron(II) with cerium(IV) salt could also be monitored (Fig. 7). It could seem probable that in these sensors, a function of carbon powder is predominant and the sensor behaves as an inert (carbon) redox electrode; however, no potential break was recorded in titrations of iodine with sodium thiosulfate.

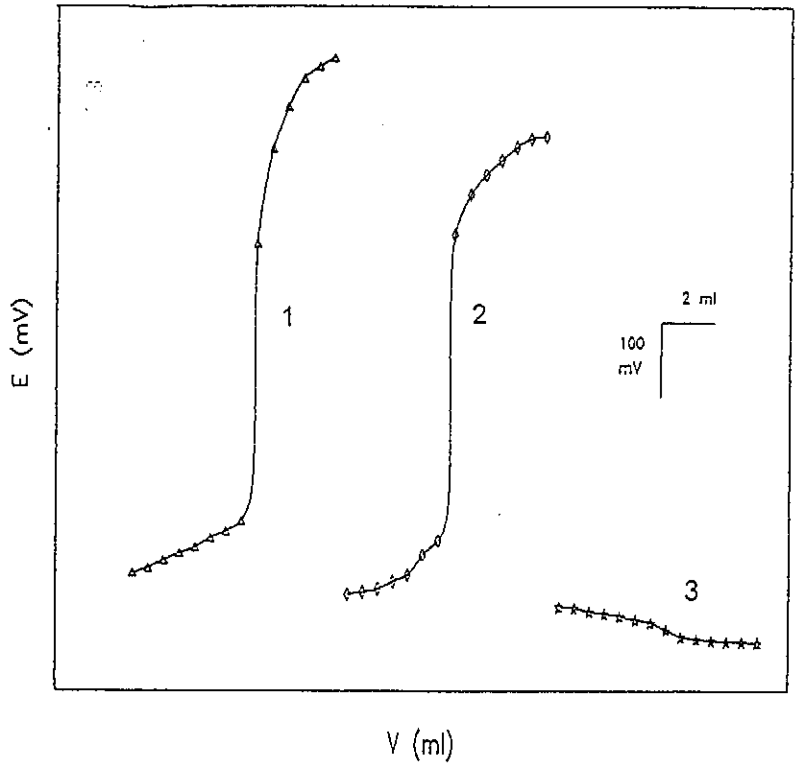

Fig. 7 Oxidation-reduction titrations monitored with the help of a CPE. (1) Iron(II) sulfate (ca. 0.35 mmol) titrated with 0.0823 M cerium(IV) sulfate; (2) iron(II) sulfate (ca. 2.5 mmol) titrated with 0.102 M potassium permanganate; (3) iodine (ca. 0.25 mmol) titrated with 0.101 M sodium thiosulfate

Titrations Based on Other Principles

Possibilities of CPEs as titration indicators were also tested in precipitation and complex formation-based titrations [40]. A well developed titration break of approx. 200 mV was obtained in titrations of chloride with silver(I) nitrate. In titrations of chloride with mercury(II) and of nickel(II) with EDTA disodium salt, a CPE sensor did not response to changes in concentrations of species involved.

Conclusion

Rather, the experiments give evidence that both CWEs and CPEs are most widely applicable to monitor titrations based on ion-pair formation, and that their use in determinations based on other principles is somewhat limited.

Anyway, there are still many questions to explain their behaviour. For example, why commercial nitrate electrode (in contrast to other sensors used with similar membranes) did not afford any potential break in acid-base titrations: this could be explained by the presence of small amount of lipophilic tetraphenylborate inside of the membrane thus resulting in a similar effect like during addition of a surfactant to the sample as discussed above. However, difficultly to explain why, in contrast to other authors [46,47] as well as to the results obtained with a CPE, we were not able to record potential breaks in titrations of iron(II) with dichromate, etc.

From the viewpoint of CWEs, sometimes a support material can also influence the resulting electrode behaviour. When platinum wire stored in sulfuric acid was coated with the membrane instead of the Pt wire exposed to the reduction force of hexacyanoferrate(II), the base line potential was shifted to more positive values about 170 mV [55]. Some results also indicate that reducing or oxidizing species, if present in the real samples, can diffuse through the membranes and cause a potential change because of their reaction with a support. As a possible solution, stabilization of the membrane redox potential by direct addition of organic oxidation-reduction systems, e.g., an ion-exchanger mixture containing Fe^{3+}/Fe^{2+}, was suggested [56]. However, numerous additional studies have to be done not to express the conclusions which could be rather disputable.

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