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Polarography in Organic Media

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Brief consideration is given to fundamental aspects—the technique of a polarographic experiment in an organic medium, factors producing a change in polarographic behaviour when water is replaced by an organic solvent, and specific features of the polarographic behaviour of inorganic and organic depolarisers—and a list of 42 references is included.

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1. INTRODUCTION

Polarography was discovered in 1922 by the well known Czechoslovak Nobel prizewinner J. Heyrovský during the investigation of aqueous solutions. This method yielded much valuable information on the mechanism and the kinetics of electrode processes in aqueous media. But soon after the discovery it became necessary to use the method also to investigate solutions in mixtures of water with organic solvents and in pure organic solvents. The original reason was the limited solubility in water of many organic and inorganic substances (e.g. elementary sulphur), whose polarographic behaviour was of interest. At the present time, however, the use of organic solvents in polarography is dictated also by the valuable information on the mechanism and kinetics of electrode processes and on the properties of solutions obtainable by working with organic solvents. The elucidation of the mechanism of the electrochemical reduction and oxidation of many classes of organic compounds, the generation and investigation of the radical-ions of organic and inorganic substances (oxygen, sulphur), the establishment of the differentiating action of organic solvents for strong inorganic acids, and other surprising results obtained with organic solvents struck the imagination and initiated a powerful new stream of investigations on these lines. It is therefore of interest to examine some fundamental aspects of the use of organic solvents in polarography. More detailed, specific information will be found in numerous reviews and also in a monograph [1].

2. EXPERIMENTAL TECHNIQUE

The development of polarography in organic media has been stimulated by advances in the chemistry and electrochemistry of organic solvents and solutions in them [2-5], by the preparation of new organic solvents having very interesting properties (propylene carbonate, an aprotic solvent having a high dielectric constant; hexametapol, in which solvated electrons exist for quite a long time; etc.), and by the production of new polarographic apparatus, especially potentiostatic instruments, which enable perfectly satisfactory polarograms to be recorded with poorly conducting solutions.

Considerable experience has accumulated of working with organic solvents. The purity of the supporting electrolyte is of primary importance for polarography in organic media. In practice it must be freed mainly from contamination with electrochemically active substances (depolarisers) and proton-donors, in particular water, if the experiment is to be conducted under aprotic conditions. On storage the purified solvents again accumulate undesirable impurities as a result of their hygroscopicity and decomposition. It is therefore advisable to work with freshly purified solvents. In some solvents peroxy-compounds, which give sharp reduction waves, appear on storage. Oxolan, for example, is best freed from peroxides by being boiled with potassium permanganate [6].

Oxygen is usually more soluble in organic solvents than in water, and is more difficult to displace from organic media than from aqueous solutions. The rate of expulsion of dissolved oxygen is increased by passing fine bubbles of an inert gas through the solution; this is achieved by inserting porous glass plates at the gas inlet into the cell. Nitrogen and electrolytic hydrogen from cylinders must be freed from traces of oxygen by combustion over catalysts or adsorption on metallic copper or other adsorbent. It is considerably more convenient to use argon, which requires no further purification, since its oxygen content lies within permissible limits. Sulphate is not employed to remove oxygen from solutions in organic solvents, since either it is sparingly soluble or it reacts slowly with oxygen.

The solvents are rigorously dried by means of powerful drying agents—alkali metals, molecular sieves, electrolysis, etc.—followed by fractionation under reduced pressure and in an inert atmosphere to avoid decomposition and oxidation, especially with high-boiling solvents.

Water of crystallisation in a salt used to prepare the supporting electrolyte or as depolariser may seriously moisten the electrolyte and nullify all efforts to dry the solvent. The salt must therefore be dried no less thoroughly. It is very difficult to remove the last traces of moisture from salts. The latter must be heated in the presence of strong drying agents in a vacuum for a long time or else melted preferably in a vacuum. But not all salts are completely freed from moisture by vacuum melting (lithium perchlorate, for example, still contains 0.1% of water [7]). Where maximum dryness is required

during an experiment, therefore, it is useful to treat the final electrolyte with such drying agents as molecular sieves or alkali metals. Salts of strongly hydrolysed multivalent metals (titanium, zirconium, hafnium, thorium, aluminium, etc.) are difficult to dry, since they decompose on dehydration of the crystalline hydrates, with formation of sparingly soluble oxy-salts. In such cases either the behaviour of the hydrates is studied [8] or the anhydrous salts are prepared under conditions excluding access of moisture.

The dehydrated solvents and solutions rapidly absorb moisture from the surroundings. It is therefore best to conduct all operations with them in an atmosphere of a dry inert gas in hermetically sealed boxes.

The water content of solvents and solutions is most often determined by titration with the Karl Fischer reagent. The Reviewer's experience has shown that water can be determined considerably less laboriously and no less accurately from the volume of hydrogen evolved on contact of a portion of the solution with calcium hydride [9]. A very sensitive ($\ll 0.01\%$) method proposed [10] for the determination of water is based on its reaction with lead tetra-acetate, the precipitated lead dioxide being estimated spectrophotometrically. Pure calcium carbide is required for the determination of small concentrations of water by gas–liquid chromatography.

The above procedures enable solutions to be prepared whose water content can be lowered to 10^{-4} M or below. In most cases, of course, such rigorous drying of the solutions is not required, since even large quantities of water by no means always effect the polarograms. The radical-anion of piazthiole, for example, is protonated by water so slowly that, in admixture with dimethylformamide, the first reduction wave of piazothiole to the radical-anion still remains completely unchanged even with water contents up to 40 vol.%, [11] and this case is by no means exceptional. The insensitivity of many electrode processes to traces of moisture enables us to work with organic solvents under ordinary laboratory conditions. Since many methods of pretreating solvent, salts, and solutions are laborious, they must be applied only where necessary.

Quite often, however, the whole arsenal of means must be used for removing moisture from the solutions. If the depolariser reacts with water, the presence of traces of moisture will lower its concentration and produce other complications. Dessy et al. [12] pointed out the need for careful drying of aprotic solutions for this reason in the investigation of organometallic compounds. Experimental conditions of maximum dryness are extremely desirable also because they may lead to the detection of radical species and also unusual valency states of elements that are otherwise too unstable.

In the choice of salt for the preparation of supporting electrolytes it is quite insufficient to assess solubility from the dielectric constant ϵ of the solvent. Experience shows that solubility and solvation often depend not only on the polarity of the solvent molecules but also on specific interaction of the ions with the solvent. The relatively non-polar pyridine ($\epsilon = 12.5$), for example, is a fairly good solvent for ionic salts, whereas formamide ($\epsilon = 113$) is comparable only with pyridine in solvent power, but is inferior to water [8].

Cations are solvated by coordination with electron-donor solvent molecules (whence the high solubility of salts in pyridine), whereas anions, which themselves are electron-donors, may be solvated by electron-acceptor solvent molecules or by hydrogen-bonding. Since hydrogen bonds are weaker than bonds in the solvates of cations, the nature of the anion strongly influences the solubility of the salt as a whole. The solubility of halides falls on passing from iodides to chlorides, while fluorides are usually sparingly soluble. Perchlorates, nitrates, nitrites, and thiocyanates are more soluble, whereas sulphates, carbonates, phosphates, oxides, and sulphides are in general insoluble [8].

Lithium perchlorate and chloride as well as tetra-alkylammonium iodides and perchlorates, which are very soluble, are most often used as supporting electrolytes in organic solvents. The maximum potential range within which mercury is polarised ideally (the polarographic range) is provided by a tetra-alkylammonium perchlorate. Thus with tetraethylammonium perchlorate in dimethylformamide we can work at potentials from +0.45 to −2.8 V relative to the saturated calomel electrode (s.c.e.). [8] This supporting electrolyte is interesting also because it exhibits the least tendency to form ion-pairs with radical-ion products of electrode reactions.

The electrical conductivities of the best electrolytes in organic solvents are considerably inferior to those of aqueous solutions. An optimum salt concentration, ensuring maximum conductivity of the solution, exists for most solvent–salt pairs. This concentration is usually close to molar, which it is desirable to ensure. With a solvent of low ionising strength, nevertheless, even fairly concentrated salt solutions are comparatively poor conductors, since a considerable proportion of the ions are combined as ion-pairs, and are not involved in the transport of current through the electrolytes. For this reason it is difficult to work with anhydrous solvents such as oxolan and dioxan.

It is often necessary to correct the polarograms for the voltage drop iR in the solution. This is best done by calculating the resistance R of the cell at the required instant t in the life of the drop from the resistivity ρ of the electrolyte [13]:

$$R = \frac{0.191\rho}{m^{1/3}t^{1/6}} \qquad (1)$$

where m (g s^{-1}) is the rate of efflux of mercury from the capillary. A reversibly dischargeable pilot ion, whose half-wave potential $E_{\frac{1}{2}}$ is independent of its concentration, can be used [14]. Inclusion of a Luggin–Haber capillary in a potentiometric cell, e.g. in work with a potentiostatic polarograph, can eliminate only part of the voltage drop, since the latter is largely concentrated near the mercury drop [13]. Rather better elimination can be achieved by arranging auxiliary, indicator, and standard electrodes in that order in a straight line.

Potentiostatic polarographs completely eliminate the effect of instability of the potential of the mercury floor as auxiliary electrode, which is especially marked in the presence of perchlorates. When polarograms are recorded by means of the usual polarograph, the potential of the indicator electrode relative to a reliable reference electrode must be measured periodically, and the polarogram must then be replotted on a linear potential scale, in order to avoid stretching of the waves and the appearance of spurious inflections, falls in current, and hysteresis phenomena.

Various electrodes of the first or second kind are used as reference electrodes, either in the test solution or externally. Very often an external aqueous calomel electrode is employed. A diffusion potential of unknown magnitude appears at the junction between aqueous and non-aqueous solutions. This is of no importance when the behaviour of different compounds in the same solvent is

compared, but it prevents a quantitative comparison of the behaviour of a given depolariser in different solvents. In this connection an electrode of the second kind may be useful, e.g. a silver chloride electrode placed in a saturated solution of a salt having a common anion (chloride). The potential of such an electrode will be independent of the composition of the medium, since the activity of the potential-determining ion will remain constant [15,16].

Several redox systems having large, weakly solvated, univalent cations, whose potentials can be regarded to a first approximation as independent of the nature of the solvent, have also been proposed for this purpose. On Pleskov's suggestion [17] the potential of the Rb/Rb^+ electrode is taken as standard, but Strehlow introduced the ferrocene–ferricinium and cobaltocene–cobalticinium systems [3,18], of which the former has become more widely used. It must be borne in mind, however, that the potential of such an electrode is only approximately independent of the nature of the solvent. The use of such systems to reveal fine effects is therefore inadmissible. In aqueous–alcoholic solutions, for example, the limiting current of the ferricinium ion changes not only with the viscosity η of the medium but also with the degree of solvation [19].

By means of such standard systems it has been established that the liquid junction potential between an aqueous saturated calomel electrode and acetonitrile, propionitrile, isobutyronitrile, phenylacetonitrile, and acetone is 0.25 V, which must simply be subtracted from the potential measured in the organic solvent relative to the aqueous reference electrode [20].

One of the most important properties of an organic solvent for polarography is its proton-donor activity. On this principle solvents can be classified as protic, aprotic, and non-protic [21]. Solvents which are proton-donors can be divided into three groups: (i) hydroxylated solvents include water, alcohols, glycols, and phenols; (ii) protogenic solvents are considerably stronger acids than water; and (iii) protophilic solvents are considerably stronger bases than water. Aprotic solvents possess neither acidic nor basic properties by definition, but in fact, with the exception of pyridine and similar compounds, they (dimethylformamide, dimethyl sulphoxide, acetonitrile, oxolan, etc.) exhibit nevertheless weak acidic or basic properties. For example, dimethyl sulphoxide is a considerably weaker acid than water, but is comparable with it in basic strength. Finally, non-protic solvents contain no hydrogen at all in their structure (sulphur dioxide, carbon tetrachloride) and cannot act as Brønsted acids, but exhibit Lewis acid–base properties.

3. CAUSES OF CHANGE IN BEHAVIOUR OF DEPOLARISERS ON PASSING FROM AQUEOUS TO ORGANIC MEDIA

Several factors influence the change in polarographic behaviour on passing from aqueous solutions to solutions in organic solvents.

1. Since the mercury-solution interfacial tension depends on the composition of the latter, change of solvent affects the drop time τ of the electrode. The effect of τ on the limiting diffusion current i_d is fully represented by the Ilkovič equation and its modifications. The change in τ may have some effect on the half-wave potentials of irreversible waves.

2. The viscosity of the medium changes on passing to another solvent, and this entails a change in diffusion coefficients. It is easy to show by means of the Ilkovič equation and the Stokes–Einstein equation ($D = kT/6\pi\eta r$) that

$$i_d \eta^{1/2} r^{1/2} = \text{const}. \qquad (2)$$

Systematic data on the effect of solvent composition on the limiting diffusion current through variation in diffusion coefficient will be found in Schwabe's publications [22–24]. Change in diffusion current is usually produced by changes not only in viscosity but also in solvation of the depolariser particles r.

3. Replacement of the solvent affects the acid–base and other equilibria in the solution (solvation, association, complex formation). This effect has many important consequences.

(*a*) Acids and acidic components of buffer mixtures are usually weaker in organic solvents, and the pH is higher. The half-wave potential of a reversible reduction wave involving ν hydrogen ions and n electrons becomes more negative [22–24]:

$$\partial E_{1/2}/\partial \mathrm{pH} = -59.1 \frac{n}{\nu}. \qquad (3)$$

(*b*) If the depolariser becomes less strongly solvated, the reversible reduction wave undergoes a positive shift, whereas weakening solvation of the product produces a shift in the opposite direction along the potential axis. The energy of interaction with the solvent depends on the dielectric constant ϵ of the medium and the particle size r. From the Born equation the standard reversible discharge potential of cations can be written [25]

$$E_0 \simeq E_{1/2} \simeq A + eZ/2r\epsilon. \qquad (4)$$

If r is assumed to be independent of the composition of the medium, i.e. if we neglect the role of specific interaction between cation and solvent, it follows from Eqn. (4) that the half-wave potential should become less negative with decrease in dielectric constant, while the product $E\frac{1}{2}\epsilon$ remains constant. In practice, however, this product is rarely constant: strictly speaking, the product $E\frac{1}{2}\epsilon r$ should be constant. Weakening solvation of the depolariser diminishes the degree of irreversibility: processes quite often occur reversibly in organic solvents that are completely irreversible in aqueous solutions [8].

(*c*) Ionic interactions are strengthened by weakening solvation of the cations of the supporting electrolyte. Much experimental information has accumulated on the effect of the nature and concentration of these cations on the reduction waves of aromatic hydrocarbons in aprotic solvents, which is governed by the formation of ion-pairs with radical-anions and dianions of the hydrocarbons [26–30]. The formation of ion-pairs displaces the waves to less negative potentials. The effect is greater the higher the charge on the hydrocarbon anion ($R^{\cdot-}$ or R^{2-}) and the cation of the supporting electrolyte, the smaller the crystallographic radius of the cation, and the higher its concentration. It is supposed that the radical-ions do not interact with tetra-alkylammonium cations; dianions interact most strongly with lithium ions. Multiply charged cations produce a very large displacement of the waves even at low concentrations: thus 0.002 M $Nb(ClO_4)_3$ displaces the half-wave potentials of the first and second waves in 0.003 M quinone in acetonitrile by 550 and 950 mV respectively [28]! Both this phenomenon and solvation are analogous to complex formation, and the composition p of the ion-pair and its equilibrium formation constant K_{eq} can be calculated from the displacement

of the half-wave potential by means of the equation[28]

$$(E_{1/2})_{cat} - (E_{1/2})_0 = \frac{RT}{F} \ln K_{eq} + \frac{RT}{F} p \ln [M^+] \quad . \qquad (5)$$

For example, the radical-anion of anthraquinone forms a 1 : 1 complex with lithium ion in dimethylformamide, having Keq = 39 M^{-1}, whereas the dianion associates with three lithium ions[28].

4. Adsorption of the solvent on the mercury may retard tangential movement of the electrode surface, and thus eliminate polarographic maxima, which are suppressed e.g. by aliphatic alcohols[22,31]. Adsorption of the solvent can in principle inhibit electron transfer.

5. An organic solvent diminishes the adsorbability of other substances, primarily organic, and is thereby able to produce various effects.

(*a*) Surface-active substances, which suppress polarographic maxima in aqueous solutions, are largely ineffective in organic solvents. In order to eliminate tangential movement in the latter, therefore, use must be made of such strong surface-active agents as dodecyl sulphate, dodecylamine hydrochloride, dodecylammonium dodecyl sulphate, octadecyl sulphopropionate, etc.[8]

(*b*) Weakening of the adsorption of depolariser and reaction product in reversible systems leads to the disappearance of adsorption waves preceding and following Brdička waves.

(*c*) With self-inhibition due to the adsorption of depolariser or reaction product, the weakening of adsorption in organic solvents leads to an increase in current, i.e. to elimination of the self-inhibition effect[32].

(*d*) Weakening of adsorption of the depolariser produces a cathodic shift in irreversible reduction waves[22-25,33].

(*e*) Kinetic and catalytic surface waves undergo greater changes in organic solvents also because of decrease in the surface concentration[33].

(*f*) In several cases the decrease in adsorbability changes the mechanism of the process. Stradyn' and Kravis have shown that, in alkaline aqueous–ethanolic solution, the first four-electron wave of nitrobenzenes separates into one- and three-electron waves. The splitting of the wave is caused by insufficiently rapid protonation of radical-anions in the surface layer of solution owing to their desorption[34].

(*g*) Elimination of adsorption phenomena by organic solvents improves the correlation between half-wave potentials and substituent constants, and permits more accurate establishment of the composition and stability of complexes with ligands that from aqueous solutions are adsorbed on mercury.

6. Organic solvents influence the structure of the electrical double layer. This undoubtedly affects the kinetics of electrode processes involving slow discharge.

4. INORGANIC DEPOLARISERS

In many organic solvents alkali-metal ions are reduced reversibly. Only the lithium ion, the most strongly solvated, exhibits some irreversibility[35]. Most bivalent cations are Lewis acids, and can be solvated by a basic solvent. In aprotic solvents they are more weakly solvated than in water, and are reduced more easily[20].

Readily hydrolysed multiply charged ions (Ti^{4+}, Th^{4+}) are reduced considerably more easily in acetonitrile than in water. Whereas in aqueous solutions the waves are attributed to the discharge of water molecules constituting the hydrate sheaths of ions, with the evolution of hydrogen, in acetonitrile thorium, for example, forms an amalgam, though not in high yield[8].

Many anions are stabilised in protic solvents by hydrogen bonds. This possibility does not arise in aprotic solvents. Therefore the activity of anions is higher in such solvents than e.g. in water. Anions may be stabilised in aprotic solvents by interaction with a Brønsted acid (HX^{2-}) or with a Lewis acid, i.e. with cations. The stability of anion–cation complexes is considerably greater in aprotic solvents than in water. This is evident from the cathodic shift in the anodic dissolution potential of mercury. Thus on passing from water to acetonitrile with an anion concentration of 0.001 M this potential shifts from 0 to −1.16 V in the presence of the hydroxide ion, from −0.1 to −0.71 V in the presence of the iodide ion, and from +0.1 to −0.61 V in the presence of the chloride ion[20].

An especially interesting result was obtained for the reduction of oxygen in aprotic solvents. Polarography cyclic volt–ammetry, and electron spin resonance established that in dimethyl sulphoxide the first stage consists in transfer of a single electron to the oxygen molecule with formation of a superoxide radical-anion $O_2^{\cdot-}$. This highly reactive species is quite stable in aprotic solvents. It is curious that the electron is transferred almost reversibly under these conditions, whereas in aqueous solutions transfer of the first electron is assumed to be the limiting stage[36].

On platinum, graphite, and gold electrodes in dimethyl sulphoxide, oxolan, and dimethylformamide elementary sulphur S_8 also undergoes one-electron reduction with formation of the radical-ionic species $S_8^{\cdot-}$, which is stable for several days[37]. Sulphur reacts with mercury to form mercury sulphide. The mechanism of the reduction of sulphur is therefore different at a dropping mercury electrode.

It is remarkable that strong mineral acids are differentiated in solvents, such as acetonitrile, that are weaker bases than water and dimethyl sulphoxide. Perchloric, sulphuric, and hydrochloric acids give identical hydrogen-evolution waves in water, but separate waves in acetonitrile, and can be determined when present together[20,21]. A linear relation exists between the pKa value of the acid in water (with p$K < 3$) and the half-wave potential of hydrogen evolution in pyridine[38].

The use of organic solvents in polarography shows promise for the analysis of metals after extraction by organic solvents without a re-extraction stage.

5. ORGANIC DEPOLARISERS

The use of aprotic organic solvents in the polarography of organic compounds has led to fundamental changes in our views on the mechanism and the kinetics of electrode processes involving them. It had previously been assumed, when many-electron and completely irreversible waves were observed in aqueous and waterlike solvents, that the limiting stage was slow transfer of the first electron. The use of aprotic solvents enabled these many-electron processes to be separated into individual elementary stages. Alternating-current polarography and cyclic volt-ammetry showed that the first electron is transferred immeasurably rapidly in organic electrochemistry, but transfer of the second electron is sometimes slow[39,40]. The irreversibility of processes in protic solvents is due to secondary chemical reactions,

mainly protonation of radical-anions and dianions. One of the few exceptions to date is the reduction of halogeno-derivatives, which is irreversible also in aprotic solvents. However, the probable cause of irreversibility even in this case is rupture of a carbon–halogen bond after or during transfer of the first electron, not slowness of the actual electron-transfer stage.

In conclusion we note that maximum accuracy of correlation of half-wave potentials with substituent constants may be ensured by the use of aprotic solvents and supporting electrolytes with cations of large radius, since only under such conditions does the half-wave potential best represent the electron affinity of the molecule. In protic solvents such correlations are complicated by preceding and following chemical reactions, as well as by simultaneous transfer of more than one electron [41,42].

It follows also from the above account that the use of aprotic solvents in a.c. polarography opens up great new possibilities for highly sensitive analysis of inorganic and organic compounds, since in many cases processes take place reversibly under these conditions.

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