APPLICATIONS OF POLAROGRAPHY IN ORGANIC ANALYSIS

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(A Review)

The polarographic analysis of organic compounds has become widespread in recent years. Published material from the Prague Conference on Polarography deals with work on the applications of polarographic methods in organic chemistry carried out up to 1951. Later publications of review nature are referred to in the articles [1-5]. A paper by A. P. Terent'ev and L. A. Ianovskaia [6] gives a complete summary of all organic compounds whose reduction has been studied up to 1954.

In the examination of the theoretical problems associated with the polarography of organic compounds, the efforts of research workers have been directed towards the establishment of the relationship between the structure of organic molecules and their ability to undergo reduction at a dropping mercury electrode. It has been shown that such reduction is possible for the majority of organic compounds which have double bonds between carbon atoms with conjugation, between carbon and nitrogen atoms, between nitrogen atoms which form part of an organic molecule and nitrogen, carbon, oxygen, etc.

It has been found that with the introduction of the groups $-CH_2I$, $-CH_2Br$, $-C_6H_5$, $-C_6H_4Cl$, $-CH_2OH$, etc. into organic molecules, the reduction potentials become more positive; the groups of atoms $-CH_3$, $-C_2H_5$, $-NH_2$, and some others, on the other hand, shift the potentials to more negative values. Molecules with a conjugated bond system have more positive reduction potentials than molecules without alternating double bonds.

A number of workers have made attempts to establish a relationship between the half-wave potential and the energy characteristics of the π-electrons of the compounds being reduced. The study of the reduction of a large number of ortho-, meta-, and para-isomers of disubstituted derivatives of benzene has led to the establishment of a relationship between the half-wave potential, the magnitude of the electron density and the activation energies for electrophilic substitution. Basu and Bhattachary [7] have suggested that the reduction of aromatic compounds at a dropping mercury electrode is determined by the change in energy of the π-electrons, and conclude that this process is similar to the process of reduction by alkali metals in alcoholic solution.

A linear relationship has been found [8] for various substituted nitrobenzenes, benzaldehydes, aromatic aldehydes and hydrocarbons, between the energies of the lowest unoccupied π-electron levels and the half-wave potentials for these compounds.

In another paper [9], a linear relationship has been established for aryl iodo compounds between the frequencies of the nuclear quadrupole interaction and the half-wave potential.

It is possible that further work in this direction will show the way to the determination of the half-wave potentials of organic compounds on the basis of data on their molecular structure.

Since many organic compounds are sparingly soluble or insoluble in aqueous media, more and more applications are being found for mixed and nonaqueous solvents. Thus anhydrous acetonitrile and dimethylformamide have been used in the reduction of benzoquinone, duroquinone, 2-methyl-1,4-naphthoquinone and other quinones. It has been found experimentally that reduction takes place in two stages: first to the semiquinones and then to the hydroquinones dianones. There are reports on the possibility of using methyl sulfonic acid as a solvent in the polarography of organic compounds. For anodic polarography using a dropping mercury electrode, A. P. Portnov

and A. M. Iakubov [11] recommend the use of supporting electrolytes consisting of caustic soda in methyl and ethyl alcohols, sodium iodide in acetonitrile and tetramethylammonium iodide in pyridine. Studies have been made on the reduction of compounds of comparatively complex structure, for example, 3-amino-3-methyl-1,2,4-thiodiazole and other similar compounds, using solutions of lithium chloride and tetramethylammonium iodide in methyl alcohol and other nonaqueous solvents as supporting electrolytes.

Important factors in the choice of a solvent are the solubility and the nature of the diffusion currents which arise at the microelectrode during the electrolysis of the organic compounds.

A reduced migration current and increased solubility are achieved by the use of ionizing solvents and indifferent electrolytes. Examples of the latter used in organic polarography include the salts of tetrasubstituted bases, lithium chloride, etc.

Considerable attention has been paid by workers in this field to the mechanism of reduction and to the quantitative determination of aldehydes, ketones, and their derivatives; methods have been worked out for analyses for special purposes, for example, the determination of aliphatic aldehydes in ether, the concentration of formaldehyde in pyrolysis products [12], the concentration of acetaldehyde in the products of acetylene hydration [13], etc. L. N. Petrova and E. N. Novikova [14] have worked out an indirect method for the quantitative determination of aldehydes in complex mixtures by precipitation with 2,4-dinitrophenylhydrazine and determination of the excess of the latter by polarographic methods. The authors have been able to determine benzaldehyde, salicylaldehyde, protocatechuic aldehyde, vanillin, piperonal and cinnamaldehyde. M. A. Romanchuk and L. G. Demina [15] have described the determination of cuminaldehyde. A polarographic method has been recommended for the quantitative determination of benzaldehyde and a number of its derivatives [16, 17]. A method has been published for the determination of unsaturated aldehydes in raw alcohol [18], etc. Particular attention has been paid to the study of the reduction of various ketones by Czech research workers [19]. A large number of methods have been worked out for the quantitative determination of derivatives of aldehydes and ketones. A method has been proposed [20] for the quantitative determination of cyclohexanedionedioxime in a buffer solution at pH = 5 after removal of dissolved oxygen. The polarographic behavior of other oximes in buffer solutions has been described in [21].

Organic acids may be determined from the magnitude of the diffusion current of the reduction of hydrogen, of the anions or of the acid molecules. The determination of certain acids which are not reduced at a dropping mercury electrode becomes possible only after they have been first oxidized. This method is also used, for example, in the determination of aromatic hydrocarbons via their nitration products, of unsaturated hydrocarbons via their halogen derivatives, etc. Descriptions have been given in the literature of the reduction of salicylic acid and its methyl ester, benzoic acid [22], dialkyl phthalates, phthalic anhydride, α-ketoacids [23], ascorbic acid [24, 25], phthalic acid and its esters [26]. Considerable interest has been attached to the reduction and simultaneous quantitative determination of acetylenedicarboxylic and maleic acids [27], maleic and fumaric acids, and also mixtures of mesityl oxide, cinnamic acid and fumaric acid [28-30].

A. L. Markman and E. V. Zinkova [31] have studied the reduction of a number of acids with cis- and trans-forms, for example: crotonic, cinnamic, mesaconic acids, etc. Buffer solutions with a pH of approximately 4.8 in 50% alcohol are recommended for the determination of mesityl oxide.

Many organic substances are oxidized at a mercury or platinum microelectrode and produce clearly-defined, readily reproducible diffusion currents. For example, 2,5-dihydroxybenzoic acid [32] gives a polarographic anodic oxidation wave similar to the diffusion wave for hydroquinone, but displaced to more positive potential values.

M. I. Bobrova and A. N. Matveeva [33] have studied the reduction of simple vinyl esters and of a number of esters in which the carbonyl double bond is conjugated with an ethylenic double bond, for example: methyl acrylate, methyl and butyl methacrylates, etc. A method has been worked out for the polarographic determination of methyl methacrylate and a stabilizer – hydroquinone – in the monomer [34, 35]. A polarographic method of analysis has been used for the study of the kinetics of polymerization processes for the case of methyl methacrylate [36].

Descriptions have been given in the literature of the necessary conditions for the polarography of ethyl nitrate, ethyl nitrite [37] and nitroglycerine [38].

Aqueous, nonaqueous and mixed solvents have been used in the reduction of halogen derivatives of organic compounds. From the large number of organic halogen derivatives whose reduction has been studied in recent years, mention may be made of carbon tetrachloride and allyl halides [39, 40]. A. V. Riabov and G. D. Panova [41] have used a polarographic method of analysis for the quantitative determination of a large number of unsaturated compounds. In the method recommended, the unsaturated compounds are first brominated to the mono- and di-derivatives, and afterwards determined polarographically. E. S. Levin and Z. I. Fodiman [42] have made a detailed study of the reduction of the chloro-derivatives of benzene, mono-derivatives of naphthalene and a number of iodobenzenes, whose half-wave potentials lie in the region of −1.5 v. Descriptions have been given in works by other authors of the reduction and quantitative determination of γ-hexachlorocyclohexane and other chlorine-containing insecticide − fungicides [43].

A polarographic method for the determination [44] of hexachlorocyclohexane employs an aqueous acetone solution containing lithium chloride as supporting electrolyte. The diffusion currents are measured at −0.7 and −1.7 v after removal of dissolved oxygen from the solution. The diffusion wave at −0.7 v corresponds to the reduction of the heptaisomers, while that at −1.7 v corresponds to the sum of the hepta- and γ-isomers.

Standard solutions of these substances are sued for the construction of calibration curves.

Reports have been given of the reduction conditions and the quantitative determination of chloroacetic acids [45] and the halogen derivatives of other acids [46]. Buffer solutions have been recommended for the determination of chloroacetone, bromoacetone and iodoacetone separately and in mixtures [47].

Experimental studies have been made of the reduction of organic compounds with a quinoid structure, and also of their derivatives [48-50]; the results of studies on such compounds have been used for their quantitative determination [51-53].

V. I. Dmitrieva and V. D. Bezuglyi [54] have developed a method for the determination of hydroquinone in methyl methacrylate on a supporting electrolyte consisting of alcohol, water, methyl methacrylate and 2% ammonium nitrate. Under these conditions the hydroquinone current is separated sharply from the support current.

The very large number of studies carried out on the behavior of organic nitro compounds at a dropping mercury cathode has made it possible to provide fairly convincing proof for the stepwise character of the reduction of a large number of nitro derivatives and to establish the nature of the various intermediate products. Thus it has been proved, for example, that phenylhydroxylamine is formed during the reduction of nitrobenzene in acid solutions. Studies have also been made of the reduction of paradinitrobenzene, dinitrotoluene, 2,5-dinitroanisole, 2,5-dinitrophenol [55] and other nitro compounds.

A combination of a polarographic method with a chromatographic separation has made possible the successful solution of the extremely difficult problem of determining the components of mixtures of 2,4-dinitrobenzene, orthonitrochlorobenzene and paranitrochlorobenzene [56], nitroaniline and nitrophenol [57], metadinitrobenzene and nitrobenzene, etc. Study of the reduction of polyhalogeno derivatives of nitrobenzene has shown that their separate determination is not always possible, because of the overlap of their reduction potentials. In [58], for example, a method is given for the polarographic determination of 2,3,5,6-tetrachloronitrobenzene in the technical product. Solutions containing acetic acid, sodium acetate, acetone and isopropyl alcohol are used for the analysis. Small quantities of 2,3,4,6-tetrachloronitrobenzene and 2,3,4,5,6-pentachloronitrobenzene interfere in the determination since these compounds have reduction potentials very close to that of 2,3,5,6-tetrachloronitrobenzene. It has been established that aliphatic nitrocompounds give clearly-defined diffusion waves on reduction at a dropping mercury electrode in the presence of lanthanum salts [59]. The polarography of substituted nitrothiophenes containing the following groups as substituents: $-CH_3$, $-CH(OCOCH_3)$, $-CH_2{=}NOH$, $-C(CH_3){=}NOH$, $-COOH$, $-COCH_3$, $-CN$, $-CHO$, $-COOC_2H_5$ and $-I$ has been described in [60]. The authors have shown that it is possible to determine quantitatively a number of compounds in mixtures of the nitration products of various thiophene derivatives. Alcoholic buffer solutions are recommended for the polarographic determinations.

Descriptions have been given of the quantitative determination of a number of nitro compounds, in particular the reduction of 1-nitroso-2-naphthylamine, 1-nitroso-2-naphthol [61], etc. Studies have been made of the reduction of azoxybenzene [62] and diazonium salts [63].

The reduction of dimethyl-, piperidine- and phenyl-N-nitrosoamines [64] takes place at comparatively low potentials at a dropping mercury electrode with one diffusion wave. A direct proportionality is observed between the value of the diffusion current and the concentration.

A study has been made of the use of a polarographic method for the detection and quantitative determination of mono-, bis-,tri- and tetrakisazo dyes [65]. Their reduction potentials are too close to permit separate identification, but their quantitative determination is possible.

Studies have been made of the polarographic behavior of methyl and ethyl derivatives of N,N'-diphenylformazone [66] in methanol buffer solutions at various pH values and in neutral solutions using lithium chloride as supporting electrolyte.

M. N. Platonova [67] has given a method for the polarographic determination of acrylonitrile; the solvent recommended consists of aqueous alcohol solutions of the salts of tetrasubstituted bases. A somewhat different method for the quantitative polarographic determination of acrylonitrile has been recommended in another paper [68].

M. I. Bobrova and A. N. Matveeva [69] have established the conditions for the reduction of a large number of aromatic and aliphatic nitriles at a dropping mercury electrode.

M. K. Saikina [70] has published detailed data on the reduction of esters of phosphoric acid at a dropping mercury electrode, and this has enabled a method to be worked out for their quantitative determination.

The reduction of many organic compounds with condensed nuclei and their derivatives has been studied up to the present. Mixtures of dioxane and water, dimethylformamide, ethyl cellosolve, etc. have been used as solvents for these compounds.

The results of a detailed study of the reduction of a large number of polycyclic aromatic hydrocarbons have been described in [71]; reduction at a dropping mercury electrode was carried out on a supporting electrolyte consisting of 0.1 M tetrabutylammonium iodide or bromide in monomethyl cellosolve.

T. I. Gornykh and A. G. Pozdeeva [72] have made a detailed study of the reduction of anthracene, phenanthrene, carbazole, diphenylene oxide, and have worked out a method for analyzing the separate fractions of coal, tar. G. A. Pozdeeva [73] has used a polarographic method for the analysis of coke-oven gas, the products of the treatment of crude benzene, naphthalene in solvent naphtha, etc. V. D. Bezuglyi and N. D. Ogdanets [74] have carried out the determination of naphthalene by first nitrating it with nitric acid and then polarographing the nitro derivative in the presence of sodium acetate and methyl alcohol.

Work has been published on the polarography of organic peroxides and hydroperoxides in aqueous and non-aqueous media [75, 76].

For this type of polarography it is best to use solvents containing ethyl alcohol and sulfuric acid with concentrations of the order of 0.1-1.0 N. A few drops of 0.1% gelatin solution or 0.4% methyl red solution are added in order to suppress the maxima. The reproducibility of separate determinations is of the order of 2%. Since the reduction potentials of separate alkyl hydroperoxides are extremely close to one another, the method cannot be applied to the analysis of mixtures for the determination of each component.

Studies [77] have shown that the oxidation of organic sulfides at a platinum microelectrode leads to the formation of sulfoxides. The anodic depolarization of 2-mercaptobenzothiazole and 2-mercaptobenzimidazole may be used for their quantitative determination [78]. A. V. Kalacheva [79] has studied the polarographic behavior of tetramethylthiuramide sulfide and has put forward a method for its determination for the control of thiuram pastes in rubber manufacture. Dichloroethane is recommended as solvent and sodium acetate in alcohol as supporting electrolyte. A detailed study has been made of the catalytic activity of a large number of organic sulfur-containing compounds [80].

Polarographic studies of the reduction of organometallic compounds are of considerable interest. The behavior of compounds of nickel [81], cobalt [82] and a number of other metals has been studied. The most thorough studies have been those [83] on the reduction of organic derivatives of tin, antimony, lead, bismuth, esters of phosphonodialkyl tin and arsenic. The authors have suggested methods for the polarographic determination of a large number of organometallic compounds.

M. B. Neiman [84] has recommended an extremely convenient method for the polarographic determination of saccharin in various materials.

In recent year studies have been made of the reduction of various heterocyclic compounds containing nitrogen, oxygen and sulfur, for example: furan, flavone and their derivatives [85], thiophene [86], etc. The polarographic reduction of aromatic heterocyclic compounds of isoflavones [87] has been studied. It has been shown in [88] that the reduction of N-ethyl-, N-phenyl, N-α-naphthyl-, N-bromophthalimide and phthalyl sulfide is analogous to that of phthalimide. S. G. Mairanovskii [89] has studied the polarographic behavior of quaternary pyridinium, N-methylpyridinium, N-methyl-β-picolinium salts, etc., which are reversibly reduced with the formation of radicals. The reduction of these compounds is accompanied by catalytic hydrogen waves. Polarographic study of bipyridines [90] has shown that acetate buffer solutions are the most suitable for the quantitative determination of the compounds. Among the complex heterocyclic compounds which have been studied, mention may be made of derivatives of alkyl- and hydroxyalkylquinoxaline [91].

Other works on the polarography of organic compounds which must be mentioned include those devoted to the study of the reduction of urea and thiourea and its derivatives [92, 93], the detection and determination of glucose, the analysis of gossypol [94], the determination of diacetylthiamine and dibenzoylthiamine, and salts of ditetrazole [95], etc.

The increase in the number of works devoted to the polarographic determination of organic substances of complex structure is a result of the further development of this trend in present-day polarography.

Data have been published on the study of the reduction of a number of ketosteroids: prednisone and cortisone [96], hydrocortisone and prednisolone [97], which may be determined quantitatively by a polarographic method using an alcoholic acetate buffer solution. Oscillographic polarography [98] has been used to study the behavior of alkaloids containing tropane and piperidine nuclei [99]. The reduction has been studied and methods developed for the quantitative determination of a large number of pharmaceutical products, for example: penicillin, stypticin, santonin and bromural, narcotine and hydrastine, riboflavin , etc.

Special surveys of work in the field of the polarography of pharmaceutical products have been published [100, 101].

The data which have been presented indicate the extensive possibilities which are revealed by the use of the polarographic method of analysis for the quantitative determination of organic substances. An important and widespread technique adopted in the quantitative polarography of organic compounds is that based on the preliminary oxidation, nitration or halogenation of the organic molecules in order to convert them to a form which can be reduced. Data on the anodic polarography of a number of organic compounds indicate the considerable importance of this method in the quantitative analysis of these substances. A characteristic feature of modern methods for the quantitative polarography of complex mixtures of organic compounds is the use of different methods for preliminary separation, for example, the use of a chromatographic method of separation followed by polarographic analysis of the individual compounds. Great promise is shown by the technique of oscillographic polarography, particularly for the analysis of mixtures of organic substances.

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