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Validated spectrophotometric methods for determination of sodium valproate based on charge transfer complexation reactions

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ABSTRACT

This work presents the development, validation and application of four simple and direct spectrophotometric methods for determination of sodium valproate (VP) through charge transfer complexation reactions. The first method is based on the reaction of the drug with p-chloranilic acid (p-CA) in acetone to give a purple colored product with maximum absorbance at 524 nm. The second method depends on the reaction of VP with dichlone (DC) in dimethylformamide forming a reddish orange product measured at 490 nm. The third method is based upon the interaction of VP and picric acid (PA) in chloroform resulting in the formation of a yellow complex measured at 415 nm. The fourth method involves the formation of a yellow complex peaking at 361 nm upon the reaction of the drug with iodine in chloroform. Experimental conditions affecting the color development were studied and optimized. Stoichiometry of the reactions was determined. The proposed spectrophotometric procedures were effectively validated with respect to linearity, ranges, precision, accuracy, specificity, robustness, detection and quantification limits. Calibration curves of the formed color products with p-CA, DC, PA and iodine showed good linear relationships over the concentration ranges 24–144, 40–200, 2–20 and 1–8 μg/mL respectively. The proposed methods were successfully applied to the assay of sodium valproate in tablets and oral solution dosage forms with good accuracy and precision. Assay results were statistically compared to a reference pharmacopoeial HPLC method where no significant differences were observed between the proposed methods and reference method.

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1. Introduction

Sodium valproate (VP) (Fig. 1) chemically known as Sodium 2-propylpentanoate, is an antiepileptic used particularly in the treatment of primary generalized seizures, has a notable benefit in absence and myoclonic seizures, and is also used for partial seizures. Its actions are complex and its mode of action in epilepsy is not fully understood. VP is also used to treat the acute manic phase of bipolar disorder and for the prophylaxis of migraine [1]. The quantification of valproic acid and its sodium salt in various drug formulations and/or biological samples was addressed in numerous reports. A comprehensive profile describing different reported methods of analysis of valproic acid and its sodium salt was published in 2005 [2]. Additionally, recent analytical reports suggested the use of gas chromatography–mass spectrometry [3,4], gas chromatography-flame ionization detection [5], capillary electrophoresis with contactless conductivity detection [6] and liquid chromatography–tandem mass spectrometry [7,8]. Due to the absence of a chromophore, chemical derivatization of VP was required prior to its HPLC analysis with diode array detection [9] and fluorescence detection [10,11]. On the other hand, electrochemical analysis of the drug was carried out using selective membrane sensors [12] and adsorptive fast Fourier transform coulometric technique (AFFTC) [13]. To the best of our knowledge, only a single article could be found in the scientific literature describing the spectrophotometric determination of valproic acid and its salts. The procedure included formation of the acid chloride by heating VP with thionyl chloride at 60 °C for more than 3 h, then reaction with 2,4-dinitrophenylhydrazine, evaporation of the solvent, dissolution of the residue in sodium hydroxide and finally measurement of the color product at 500 nm. The published method showed linear correlation between absorbance and VP concentration over the range 13.65–45.45 μg/mL [14].

The interest to establish simple, fast, and adequately sensitive spectrophotometric methods to be suitable for routine analysis in control laboratories has been one of the main targets for analytical chemists. The formation of a charge transfer complex involves a transfer of electronic charge from an “electron rich” molecule to an “electron deficient” molecule. As a result, one compound becomes partially positively charged with respect to the other and a weak electrostatic bond is formed. The molecular interactions between electron donors and

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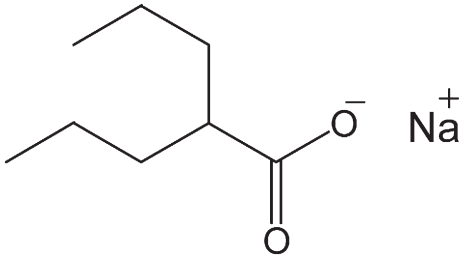

Fig. 1. Chemical structure of sodium valproate (VP).

electron acceptors are generally associated with the formation of intensely colored charge-transfer complexes, which absorb radiation in the visible region. The rapid formation of charge transfer complexes leads to their utility in the development of simple and convenient spectrophotometric methods for several pharmaceutical compounds which behave as electron donors [15–17].

Being a salt of weak acid and a negative charge carrier, sodium valproate is a good electron donor and can form charge transfer complexes with various acceptors. The same principle was followed with similar weak acid salts such as losartan potassium and rabeprazole sodium which reacted effectively with several electron acceptors, and the colored products were utilized for their spectrophotometric assays [18, 19]. The fact that up till now the charge transfer complexation reactions of VP have not been tackled yet since no analytical reports are found in the literature, encouraged us to develop simple, rapid and reliable spectrophotometric methods for the analysis of VP for quality control purposes. Such simple and direct methods of analysis are important and efficient especially in case of drugs that lack chromophores, and consequently, suffer from shortage of spectrophotometric analytical methods. The proposed methods in this work are based on the charge transfer interactions between VP as electron donor and p-chloranilic acid, dichlone, picric acid as π-acceptors and with iodine as a σ-acceptor.

2. Experimental

2.1. Instrumentation

Spectrophotometric measurements were carried out on a T80 double beam UV/VIS spectrophotometer (PG instruments Ltd., London, UK) connected to a PC loaded with UV WIN 5 software (version 5.2.0) using a pair of 1 cm matched quartz cells.

2.2. Materials and reagents

Sodium valproate (VP) was kindly provided by Global Napi Pharmaceuticals (6th of October City, Giza, Egypt). Analytical grade of 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone (p-chloranilic acid, p-CA) (BDH Chemicals, Poole, UK), 2,3-dichloro-1,4-naphthoquinone (dichlone, DC) (Sigma-Aldrich Chemie GmbH, Steinheim, Germany), 2,4,6-trinitrophenol (picric acid, PA) (S.D. Fine Chem Ltd., Mumbai, India) and iodine (Riedel-de Haën AG, Seelze, Germany) were used. All solvents and other chemicals used throughout this study were of analytical grade. The pharmaceutical preparations used in the present investigation were Depakine® tablets (Global Napi Pharmaceuticals for Sanofi Egypt S.A.E. under license of Sanofi, Paris, France, B.N. A13928), labeled to contain 200 mg sodium valproate per tablet and Depakine® oral solution (Sanofi-Aventis, Paris, France, B.N. 423), labeled to contain 200 mg sodium valproate per mL.

2.3. Preparation of VP stock standard and reagents' solutions

Stock standard solutions of VP, 800 μg/mL, 200 μg/mL and 50 μg/mL, were separately prepared in methanol to be used for the reactions with p-CA, PA and iodine respectively. Stock standard solution of VP (2000 μg/mL) was prepared in DMF for the reaction with DC. Reagents' solutions were freshly prepared in the following concentrations: p-CA (4 mg/mL) in acetone, DC (10 mg/mL) in DMF, PA (5 mM ≈ 1.2 mg/mL) in chloroform and iodine (5 mg/mL) in chloroform.

2.4. General procedures and construction of the calibration graphs

Method I: aliquots (300–1800 μL) of VP stock standard solution (800 μg/mL) were transferred into a series of 10-mL volumetric flasks. Volumes were adjusted to 2 mL with methanol and 0.6 mL of p-CA solution was added. The volume was completed with acetone and the absorbance was measured at 524 nm against reagent blank.

Method II: aliquots (200–1000 μL) of VP stock standard solution (2000 μg/mL) were transferred into a series of 10-mL volumetric flasks. A volume of 1 mL of DC solution was added. The volume was completed with DMF and the absorbance was measured at 490 nm against reagent blank.

Method III: aliquots (100–1000 μL) of VP stock standard solution (200 μg/mL) were transferred into a series of 10-mL volumetric flasks. Volumes were adjusted to 1 mL with methanol and 1 mL of PA solution was added. The volume was completed with chloroform and the absorbance was measured at 415 nm against reagent blank.

Method IV: aliquots (200–1600 μL) of VP stock standard solution (50 μg/mL) were transferred into a series of 10-mL volumetric flasks. Volumes were adjusted to 2 mL with methanol and 0.8 mL of iodine solution was added. Solutions were allowed to stand for 30 min, then completed to volume with chloroform and the absorbance was measured at 361 nm against reagent blank.

In each method, absorbance values were plotted against the corresponding concentrations to construct the calibration graph.

2.5. Assay of VP dosage forms

2.5.1. Assay of Depakine® tablets

Ten tablets were accurately weighed and finely powdered. Accurate weighed portions of the powder equivalent to 80, 20 and 5 mg VP were extracted into separate volumes of 50 mL methanol with the aid of sonication for 20 min then filtered into separate 100 mL-volumetric flasks. The residues were washed with portions of methanol and washings were added to the filtrates, then the solutions were diluted with methanol to reach final concentrations 800, 200 and 50 μg/mL VP (stock sample solutions for reactions with p-CA, PA and iodine respectively).

For the reaction with DC (method III): An accurately weighed portion of the powder equivalent to 200 mg VP was extracted into 50 mL DMF with the aid of sonication for 30 min then filtered into a 100 mL-volumetric flask. The residue was washed with portions of DMF and washings were added to the filtrate, then the solution was diluted to volume with DMF to reach a final concentration 2000 μg/mL VP (stock sample solution for reaction with DC).

Aliquots of the prepared stock sample solutions were transferred into 10 mL volumetric flasks, and the assays were completed as described under general procedures. Recovery values were calculated from similarly treated standard solutions.

2.5.2. Assay of Depakine® oral solution

A volume of 2 mL of Depakine® oral solution was transferred into 50 mL volumetric flask and completed to volume with methanol. An aliquot of this methanolic solution (10 mL) was diluted to 100 mL with methanol to reach a final concentration 800 μg/mL VP (stock sample solution for reaction with p-CA). A volume of 25 mL of the stock sample solution for reaction with p-CA was diluted to 100 mL with methanol to reach a final concentration 200 μg/mL VP (stock sample solution for

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