Electrochimica Acta 93 (2013) 272–278

Contents lists available at SciVerse ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Differential dynamic potentiometric responses obtained with anion-selective electrodes for perchlorate, thiocyanate, iodide, nitrate, sulfate, picrate and bis(trifluoromethylsulfonyl) imide

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ARTICLE INFO

Article history:
Received 10 December 2012
Received in revised form 21 January 2013
Accepted 21 January 2013
Available online 28 January 2013

Keywords:
Differential dynamic potentiometry
Ion-selective electrodes
Cyclodextrin
Anion fingerprints
Principal components analysis

ABSTRACT

Differential dynamic potentiometric (DDP) responses for perchlorate, thiocyanate, iodide, nitrate and sulfate as inorganic anions, and picrate and bis(trifluoromethylsulfonyl) imide, a common ionic liquid anion, as organic anions are presented. DDP signals were obtained as the difference between the individual potential responses displayed by two anion-selective electrodes, one containing a membrane with β-cyclodextrin (β-CD) as anion-ionophore and the other containing a similar membrane without β-CD (blank membrane). Highly reproducible DDP signals characteristic for each anion were obtained. Principal components (PC) analysis applied to the DDP responses permitted differentiation of the anions assayed. Additionally, a linear relationship was found between the PC1 values of each anion signal and the corresponding values of an anion lipophilicity descriptor. Finally, the DDP technique was extended to the study of some anion mixtures.

1. Introduction

Since the initial development of ion-selective electrodes (ISEs), their dynamic behavior has been the subject of interest for many researchers [1]. While the transient potential signals obtained for the concentration of single primary ions are quite simple and exhibit a monotonic and asymptotic character, the transient signals observed in the presence of interfering ions are more complex [2]. These include non-monotonic signals consisting of fast overshoot followed by slow relaxation and sluggish monotonic responses [3,4].

From a practical point of view, the dynamic response is important since a low response time is necessary for potentiometric measurements in flow systems and for the development of kinetic-potentiometric methods [5]. Also, a slow response may be an indicative of membrane fouling. Moreover, the transient signals obtained in ISE dynamic response studies can provide additional information useful for analytical purposes. Thus, a selectivity parameter characteristic of different ions was obtained from transient signals obtained in flow-injection potentiometry [6,7]. A variety of chemometric approaches has permitted the whole sequential-injection or flow-injection potentiometric signal obtained with ISEs to be used for qualitative and quantitative analyses [8,9]. Recently, differential dynamic potentiometric (DDP) responses obtained with an ISE couple to incrementally increasing cationic drugs concentration in batch mode have been proposed as drug-fingerprints [10].

Since the beginning of ISE dynamic studies, several theoretical models have been proposed to explain transient signals. While the first models focused on precipitated-based ISEs [1], recent models are directed towards carrier-based ISEs. Some of these are based on the assumption of local equilibrium at the membrane interface and on the lack of diffusion potential within the membrane (phase boundary potential model) [11,12], although other more elaborate models do not consider these restrictions [13]. However, both types of model allow experimental dynamic responses to be explained. Of note is the approach reported by Bakker and col. [14] which predicted the experimental dynamic responses of carrier-based ion-selective electrodes to incrementally increasing target ion concentrations.

Several aims are addressed in the present paper. First, the extension of the differential dynamic potentiometric technique (DDP) previously proposed for cationic drugs [10] to anions. Recently, different types of ionophores have been successfully used for the construction of ion-selective electrodes for several anions [15–20]. In the present paper, perchlorate, thiocyanate, iodide, nitrate and sulfate were used as inorganic anions, and picrate and bis(trifluoromethylsulfonyl) imide, a common ionic liquid anion, as organic anions. The DDP responses for these anions were obtained as the difference between the individual potential responses displayed by two anion-selective electrodes, one containing a membrane with β-cyclodextrin (β-CD) as

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0013-4686/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.electacta.2013.01.101

anion-ionophore and the other a similar membrane without β-CD (blank membrane). The second aim was to apply principal component analysis (PCA) to the DDP signals obtained, in order to differentiate between the anions assayed. A final aim was to study for the first time DDP signals for anion mixtures.

2. Experimental

2.1. Reagents and solutions

All chemicals were of analytical reagent grade and Milli-Q water was used throughout. Polyvinyl chloride (PVC) of high molecular weight, bis(2-ethylhexyl) sebacate (DOS), 2-nitrophenyl octyl ether (NPOE), tricresyl phosphate (TCP), tridodecylmethylammonium chloride (TDMACl) and tetrahydrofuran (THF) were purchased from Fluka. Heptakis (2,3,5-tri-O-benzoyl)-β-cyclodextrin (β-CD), bis(trifluoromethylsulfonyl) imide lithium salt and picric acid were purchased from Sigma. The sulfate, chloride, nitrate, iodide, thiocyanate and perchlorate used as their corresponding sodium compounds were also purchased from Sigma.

Standard solutions (10^{-1} M) of sulfate, chloride, nitrate, iodide, thiocyanate, perchlorate, and bis(trifluoromethylsulfonyl) imide anions were prepared by dissolving suitable amounts of their corresponding salts in water. Working solutions (10^{-2} and 10^{-3} M) were prepared by appropriate dilution of 10^{-1} M solutions.

To obtain a 10^{-1} M standard solution of the sodium salt of picric acid, an adequate volume of 2×10^{-1} M solution of the acid was potentiometrically titrated with 4×10^{-1} M sodium hydroxide to end point. Then, the solution was transferred to a 50 ml calibrated flask and diluted to the mark with water. Working solutions (10^{-2} and 10^{-3} M) were prepared by diluting this with water.

2.2. Apparatus and electrodes

The potentiometric response of either of two ISEs against a common reference electrode was measured by means of a three electrode system immersed in the same solution and connected to a potentiometer designed by our research group. A homemade dual channel potentiometer, a fast multiplexer, an analogical to digital converter and a PC connected in series permitted simultaneous recording of the potential of each ISE against the reference electrode. By means of appropriate software, the plots of the potential of both ISEs and of the potential difference between the two ISEs *versus* time were recorded.

Fluka ISE bodies and an Orion Ag/AgCl double-junction reference electrode (Orion 102 90-02) containing a 10^{-4} M KCl solution in the outer compartment were used.

2.3. Membrane preparation and conditioning

The compositions of the membranes assayed are resumed in Table 1. Membranes containing cyclodextrin (membranes A, C and E) were prepared by dissolving approximately 100 mg of PVC, 200 mg of plasticizer (DOS, TCP or NPOE), 3 mg of the ionic additive TDMACl and 30 mg of β-CD in 3 mL of THF. In the preparation of membranes without cyclodextrin (membranes B, D and F), the amount of the other components was the same as above. In each case, the membrane solution was poured into a Fluka glass ring (inner diameter 28 mm, height 30 mm) on a Fluka glass plate, and allowed to settle overnight until total evaporation of THF had occurred, thus providing a thin plastic membrane. A 6-mm-diameter piece was cut out with a punch for ISE membranes and was incorporated into an ISE electrode body containing 10^{-4} M KCl as internal filling solution. The electrodes were conditioned in water until they reached a constant potential. This procedure was also followed after exposure to any of the anions tested to recover the initial potential.

The electrodes were first conditioned by immersing them in water for one day, until they reached a constant potential value. Before assaying any of the anions tested the electrodes were conditioned by immersing both together in 50 ml of water, stirring the solution with a magnetic stirrer at 700 rpm until both electrodes reached their corresponding initial potential baseline ± 5 mV. This conditioning step took up to several minutes. When the electrode had previously been exposed to a very lipophilic drug, the conditioning water was discarded and renewed once to achieve the original baselines. When not in use, the electrodes were kept immersed in water.

2.4. Differential dynamic potentiometric measurements

The DDP response was defined as the recording of the potential difference between two ISEs *versus* time [10]. In the present work, an anion-selective electrode containing a membrane with β-CD together with an electrode with the corresponding blank membrane were used to obtain the DDP response.

DDP measurements were carried out at room temperature under constant magnetic stirring (700 rpm). Consecutive anion concentration steps were established by an injection program consisting of adding consecutive volumes of 5, 20, 50, 100 and 230 μl of 10^{-3} M, 20 and 40 μl of 10^{-2} M and 10 and 40 μl, of 10^{-1} M solutions of the corresponding anion using micropipettes to cover a concentration range of 1.0×10^{-7}–1.2×10^{-4} M. The duration of the first five lower concentration steps and the last four higher concentration steps was set at 5 and 3 min, respectively.

2.5. Differential dynamic potentiometric measurements of perchlorate–thiocyanate mixtures

Different 10^{-1}, 10^{-2} and 10^{-3} M perchlorate solutions containing thiocyanate in perchlorate/thiocyanate molar ratios of 9:1, 8:2, 7:3, 6:4, 4:6, 3:7, 2:8 and 1:9 were prepared. DDP signals for each of these ratios were obtained following the injection program described above.

Table 1
Composition of the membranes assayed.

Membrane	Percentage (w/w) of components in membrane					
	DOS	TCP	NPOE	PVC	TDMACl	B-CD
A	60	–	–	30	1	9
B	66	–	–	33	1	
C	–	60	–	30	1	9
D	–	66	–	33	1	
E	–	–	60	30	1	9
F	–	–	66	33	1	