The Effect of Acetate Buffer Concentration on the Anodic Stripping Voltammetric Response of Carbon Paste (Macro)Electrodes and Microelectrodes

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Abstract:

The Square Wave Anodic Stripping Voltammetry response of *in situ* deposited Bi-film conventional size Carbon Paste Electrodes (CPEs) and generic microdisc carbon paste microelectrodes (CPμEs) in Pb(II) and Cd(II) solutions, has been studied as a function of acetate buffer concentration in the extended 0.001 M -0.5 M range. The advantages of microelectrodes (high ohmic tolerance and high mass transfer rates) allowed for the recording of good quality voltammograms at the CPμEs even at the lowest 0.001 M acetate levels studied, resulted in relatively higher voltammetric peaks and gave an optimum Pb and Cd signal in the 0.01-0.02 M acetate range.

Keywords: Anodic stripping voltammetry; Carbon paste electrodes; Microelectrodes.
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Introduction

Following their introduction and parallel to the establishment of Bi film electrodes as a powerful alternative to Hg in stripping analysis [1-5] our groups have departed on a series of studies aimed at understanding the physical chemistry behind the behaviour of these electrodes and applying these findings to optimize their analytical performance [6-10].

These studies focused on the effect of Bi ion concentration (in cases of *in situ* plated films) [6,7] and acetate buffer concentration [8-10], as well as exploiting the advantages of microelectrodes [8-10]. With respect to the latter, we have shown that Bi-plated microelectrodes (either carbon microdiscs or novel carbon paste microelectrodes) can operate efficiently without stirring during the preconcentration step and with minimum amount of added acetate. In [10] we have established and interpreted in detail the optimum acetate concentration levels for Pb(II) and Cd(II) detection by anodic stripping voltammetry at C microdiscs. In a logical expansion of that work, one should also establish the appropriate acetate levels fot this detection using carbon paste microelectrodes (CPµE).

Hence, the aim of the present paper is the study of the effect of acetate buffer levels on Pb(II) and Cd(II) anodic stripping voltammetry at Bi-plated CPµEs. In more detail, its objectives have been *(i)* the application of square wave anodic stripping voltammetry (SWASV) at *in situ* plated Bi film CPµEs, in standard Pb(II) and Cd(II) solutions of various acetate buffer levels in the 0.001 – 0.5 M range and *(ii)* comparison of the optimum acetate levels for CPµEs with those for large carbon paste electrodes (CPEs).

Experimental

Electrodes

The carbon paste used was prepared by intimate hand mixing of 1.0 g graphite powder (natural and chemically purified graphite "CR-5", Maziva, Týn n.Vltavou, Czech Republic) with approximately 0.6mL highly viscous silicone oil ("SO", LUKOIL MV 800 product; Lučební závody Kolín, Czech Republic). Freshly made carbon paste mixtures were checked with respect to their ohmic resistance; all values being within the 5–50 ohm range, indicating sufficient compactness and homogeneity of the individual mixtures.

For large CPEs, the paste was packed into piston-driven carbon paste holders made in the laboratory. The carbon paste electrode surface was renewed before starting a new series of experiments or prior to analysis of each sample by extruding *ca*. 0.5mm of carbon paste from the holder followed by wiping with wet filter paper. The diameter of the carbon paste electrode was 2 mm.

For the small CPµEs, the holder was based on the lower part (ca. 2 cm long) of disposable micropipette tips (Universal tip, WPI Inc., end-tip diameter ca. 500 µm). These

were shrunk to an end-tip diameter in the 50–300 μm range by brief exposure to a hot air stream (400–450^{0}C) produced by a heat-gun (Model 1850, Beta Utensili S.r.l.). In cases that the manual heating procedure resulted in closed end-tips the latter were cut with a razor blade under a magnifying glass, to produce a micrometer size diameter opening.

The heat-shrunk holder was then packed with the carbon paste (for its composition see above) with the help of a common pin that also served as the electrical contact. The surface of the resulting CPμE was renewed between sets of measurements by further pushing the pin into the paste whereby a micrometer-sized thread of carbon paste could be squeezed out of the holder's opening and wiped with tissue paper. A photograph of the resulting microelectrode is presented in Figure 1. The diameter of the CPμEs could be checked by an optical microscope (INTRACO MICRO, s.r.o., SM 6A, Czech Republic) or by SEM (JEOL JSM-5600LV) after the electrochemical experiments. The geometric area of the CPμEs as well as their near-microelectrode behaviour was confirmed by running slow potential scan voltammograms for the reduction of ferricyanide rom 5mM potassium ferricyanide solutions in 0.1M KCl. The CPμE used in the experiments presented here had a diameter of ca 70 μm.

Fig. 1: *Photograph of the carbon paste microelectrode (CPμE), showing the plastic micropipette tip body, the carbon paste filling at the bottom of the tip and the stainless steel nail current collector immersed into the wider end of the tip and fixed with parafilm.*

Electrochemical Experiments

Bi(III) standard solutions of 10^{-4} M Bi(III) had been acidified with HNO_3 (to a 0.15 M HNO_3 level) and the required volume was spiked into the sample with a micropipette. The parameters of the SWASV experiments were: $E_{deposition}$= -1.10 V vs. SCE; E_{final}= +0.0 - +0.2 V vs. SCE; $t_{deposition}$= 300 s; $t_{equilibration}$= 15 s; frequency = 25 Hz; potential step = 5 mV; amplitude = 20 mV. To ensure complete Bi stripping before each measurement, a pulse at $E_{conditioning}$ = +1.0 V was applied for 60 s.

The CPE macro electrode or the CPµE microelectrode, a SCE (Radiometer) reference electrode and a Pt coil auxiliary electrode (BAS Inc.) were used in a 3-electrode arrangement with the help of a PGSTAT 100 Autolab, controlled by GPES version 4.8 software (Ecochimie, Utrecht, Holland). The solution volume was 50 ml and in the case of CPE magnetic stirring was employed. For pH measurements, a Radiometer Blue Line pH-meter was employed and for conductivity, a RS 180-7127 G-meter. The respective pH and conductivity values of the solutions used are given in Table 1 below.

Table I: *Experimental values of pH and specific conductivity*, σ, of solutions containing 10^{-7} M $Pb(NO_3)_2$ + 10^{-7} M $Cd(NO_3)_2$ + 10^{-6} M $Bi(NO_3)_3$ + $1.5×10^{-3}$ M HNO_3 and various amounts of acetate buffer.

$c_{acetate}$ (M)	pH	σ (mS cm^{-1})
0.001	3.03	0.57
0.01	4.22	0.83
0.02	4.47	2.14
0.1	4.70	5.60
0.2	4.75	8.79
0.5	4.75	12.96

Chemicals

Analytical reagent grade chemicals were from Merck (Damstadt, Germany) and Fluka. 1 M stock acetate buffer was prepared from concentrated CH_3COOH p.a. (Fluka) and CH_3COONa p.a. (Fluka) solutions. Solutions for *in-situ* bismuth plating, were prepared from $Bi(NO_3)_3.5H_2O$ (Merck, Germany), while $Pb(NO_3)_2$ p.a. and $Cd(NO_3)_2.4H_2O$ p.a. (Merck) were employed in the preparation of metal ion stock solutions. The 10^{-4} M Bi(III) stock solutions were acidified with HNO_3 (Fluka) resulting in stock solutions of 0.15 M HNO_3.

Results and Discussion

SWASV at CPEs and CPμEs

Figures 2 and 3 below show the SWASVs of both the conventional-large disc CPE and the generic-microdisc CPμE, in solutions of 10^{-7} M Pb(II) + 10^{-7}M Cd(II) spiked with 10^{-6} M Bi(III), for various acetate levels, starting from the lowest concentration necessary to observe an acceptable signal (0.001 M; Figures 2(A), 3(A)) and, through the moderate concentrations range (0.01 M, 0.02 M; Figures 2(B), 3(B)), ending with the highest concentration range usually employed in electroanalytical applications (0.1, 0.2, 0.5 M; Figures 2(C), 3(C)).

A couple of differences between the two types of electrodes can be readily noticed. In the solution of lowest acetate concentration, the voltammogram at the CPE is drawn-out and the observed peaks of Cd, Pb and Bi (from negative to less negative potentials) ill-defined. This may be attributed to the very low conductivity of these solutions (see Table I) and the much higher currents recorded at these electrodes (nearly 2 orders of magnitude higher from those at CPμEs, from baseline to highest peak), which result in high ohmic distortions.

This is the manifestation of one of the advantages of microelectrodes, namely that of low IR-drop, in the case of CPμEs. Second, the Cd and Pb peaks appear to be enhanced with respect to that of Bi in the case of the CPμEs. Since all other conditions (ion concentration, deposition potential and time) are the same for both types of electrodes, any relative differences should be attributed to the effect of enhanced mass transfer rates of the CPμEs (this will be further discussed in the next section).

A similarity for both electrodes is the fact that as the acetate levels increase, the Bi stripping peak is shifted towards more negative potentials. This can be attributed to an increase of the pH of the bulk solution (see Table I) as one moves from the unbuffered-acidified solution (via spiking with an acidic Bi(III) standard) to the buffered-pH~4.7 acetate medium. It has been argued in [8] (and references therein) that the formation of Bi(III)-OH complexes in non-acidic conditions, can shift the Bi oxidation to more negative potentials (*i.e.* facilitate its stripping process)
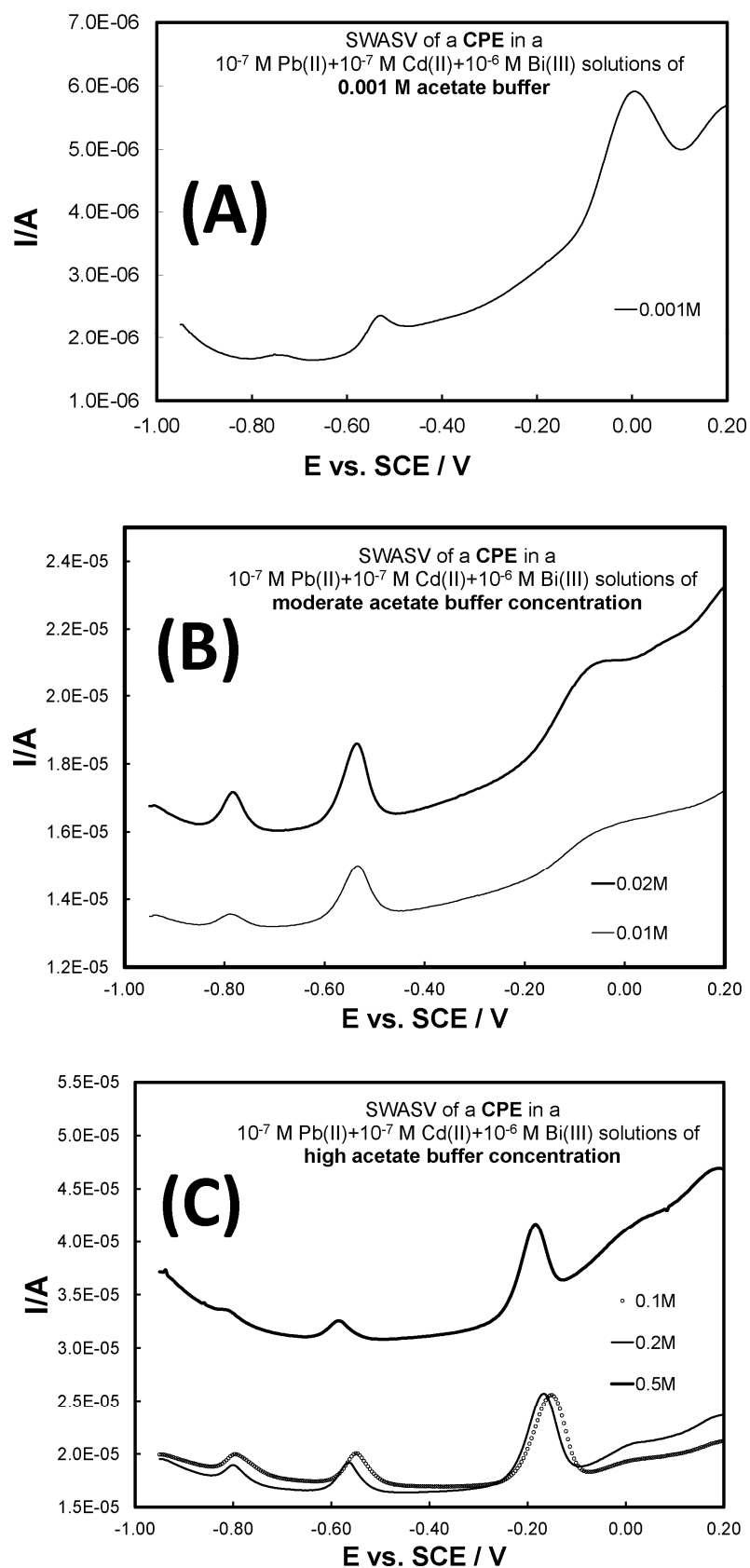
Fig. 2: *SWASV voltammograms obtained at a conventional CPE from* 10^{-6} *M Bi(III)* + 10^{-7} *M Pb(II)* + 10^{-7} *M Cd(II) solutions of varied (0.001-0.5 M) acetate buffer concentrations.*
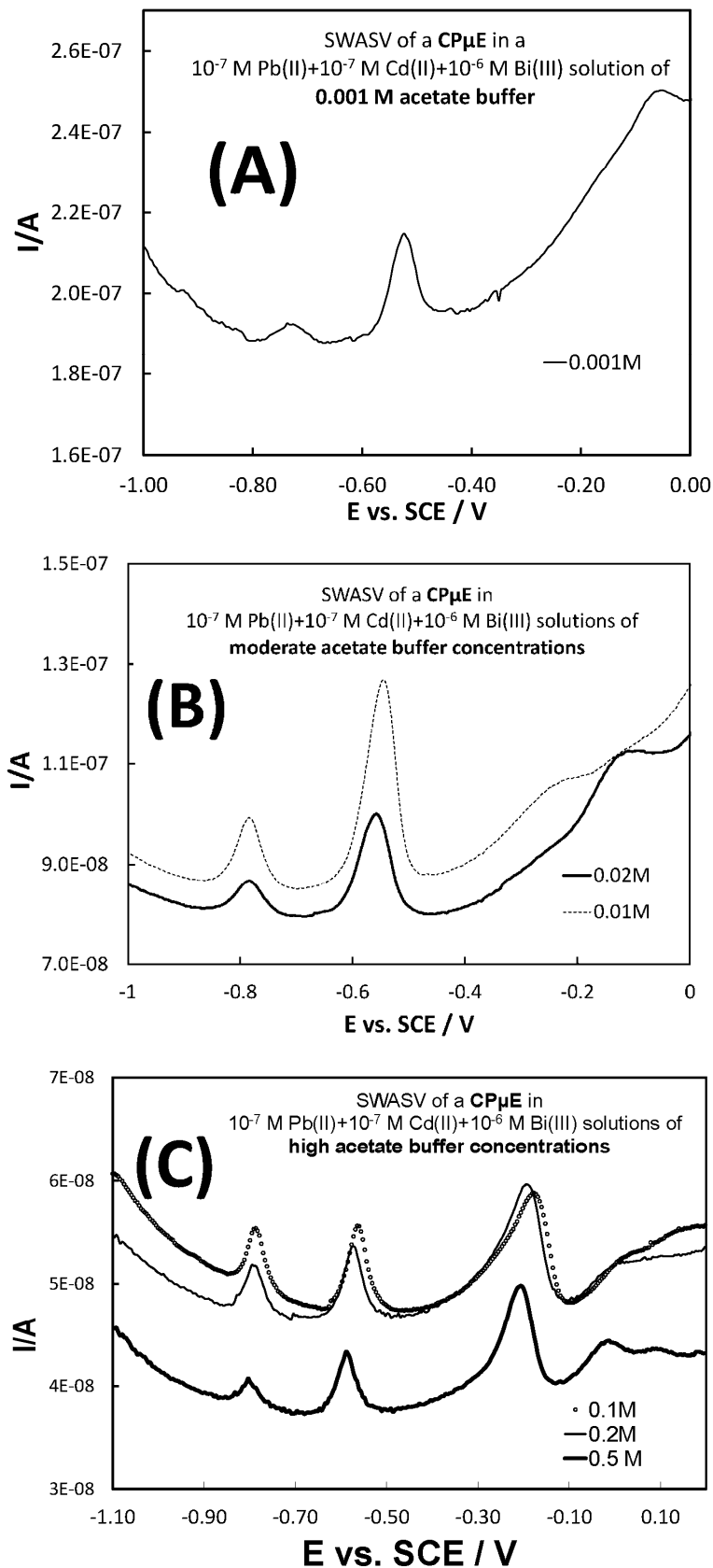
176

Fig. 3: *SWASVs obtained at a generic CPμE from* 10^{-6}M Bi(III) + 10^{-7}M Pb(II) + 10^{-7}M Cd(II) solutions of varied (0.001-0.5 M) acetate buffer concentrations.

Variation of SWASV Pb, Cd, and Bi Stripping Charge with Acetate Buffer Levels

Figure 4 presents the stripping peak charge of the two analytes and Bi at varied acetate buffer concentration. The choice of the stripping charge instead of the peak current is thought to give a more accurate representation of the stripping processes since it alliviates to a certain extent peak deformation. It can be seen that the shape of the curve for Bi is similar for both electrodes (reaching an almost constant high value above 0.1 M acetate) whereas that for Pb and Cd are strikingly different in that a pronounced maximum is observed at CPμEs for both these analytes at 0.01 M acetate.
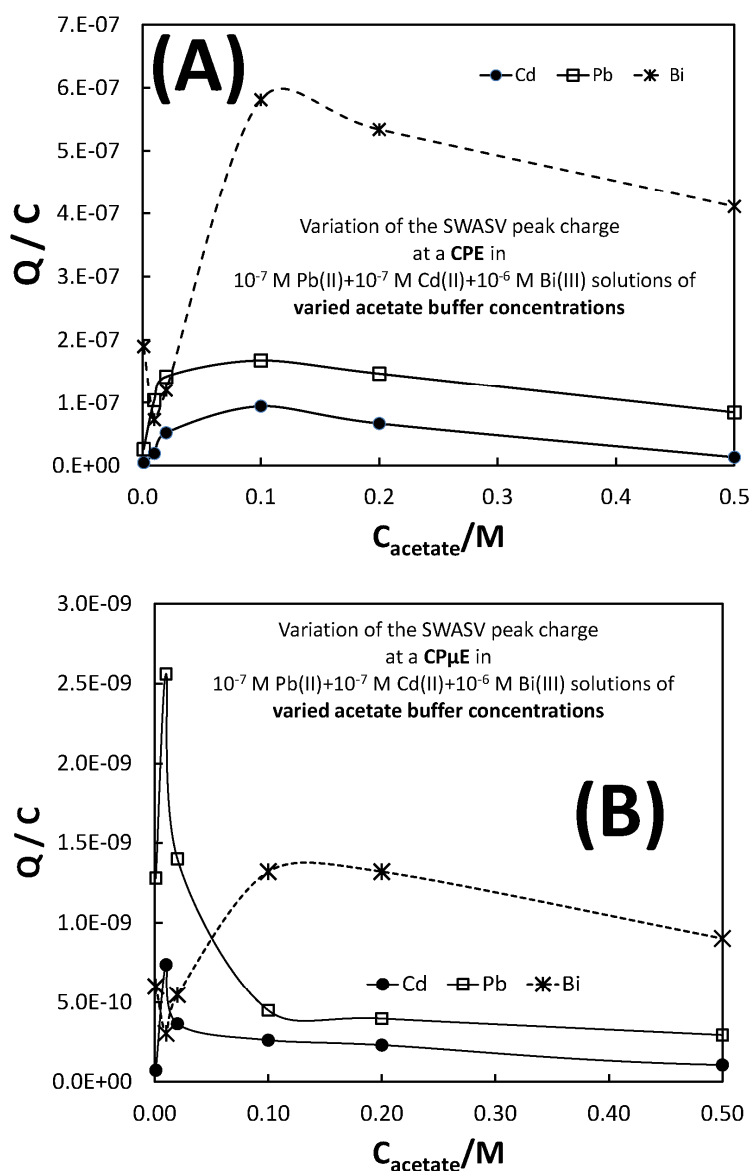

Fig. 4 *Charge corresponding to the stripping of Cd, Pb and Bi from (A) large CPE and (B) small CPμE.* SWASV experiments in Pb(II)+Cd(II)+Bi(III), as a function of acetate concentration in the 0.001-0.5 M range.

178

First, we depart on a comparison of the stripping charge values at the 0.1 M acetate buffer levels, where both the bulk solution and that in the vicinity of the electrode are and remain constant at the corresponding pH value throughout the metal ion deposition and stripping processes.

Table II presents the ratios of the stripping charges for Bi, Pb, Cd at the CPEs with respect to those at the CPμEs. It can be seen that values around 400 are observed in all cases for 0.1 M acetate, which is much lower than the electrode area ratio of ca. 816 that can be calculated based on the dimensions of the CPEs and CPμEs. This is a manifestation of the second advantage of using microelectrodes, namely that of increased mass transfer rates due to non-planar (in this case hemi-cylindrical) diffusion. These rates are translated to high Bi, Pd and Cd deposition rates, under the mass transport control conditions that prevail at the extreme negative potentials of the accumulation step.

Table II: *Ratios of stripping charges (Q) for all metals at the CPEs with respect to those at the CPμEs*. High (0.1 M) and moderate (0.01 M) acetate concentration.

Metal	$c_{acetate}$ (M)	$Q_{CPE}/Q_{CP\mu E}$
Bi	0.1	440
Pb		373
Cd		382
Bi	0.01	239
Pb		41
Cd		26

The results of the same comparison at the lower 0.01 M acetate levels (where the maxima occur for the CPμE) are different. First of all, there is a further decrease in the ratio for the Bi peak, presumably due to the fact that under acidic conditions there is more concurrent hydrogen evolution and electrode vicinity alkalization at the CPE, since hydrogen evolution is a kinetically controlled process and is favoured against mass transferred controlled processes (such as that of Bi deposition at the extreme negative potentials of the accumulation step) if the latter are not characterized by very high mass transfer rates. Both these effects are expected to decrease the quantity of Bi deposited, by a decrease in the current efficiency of the process and increased hydrolysis in the vicinity of the electrode.

Similar decreased Pb and Cd deposition current efficiencies at the CPE for 0.01 M acetate should hold but cannot explain the much lower values (41 and 26) observed. As also

argued in [10], where a significant Pb and Cd signal enhancement was observed at C microdisc electrodes in low acetate concentration solutions, the decreased levels of free acetate ions at the acidic conditions of these solutions result in low levels of Pb and Cd acetato-complexes and therefore in much higher deposition rates and stripping charges. Presumably this effect is manifested only in the case of CPμEs since in the case of CPEs it may be completely offset by the significant decrease in Bi deposition (explained before). (One should keep in mind that the basis of stripping voltammetry at Bi electrodes is the amalgamation of Bi with Pb and Cd.) One should also notice that the decrease in the Bi stripping charge as one passes from 0.1 M to lower acetate levels is more pronounced in the case of CPEs (Figure 4(A)) than in that of CPμEs (Figure 4(B)).

Finally, in an attempt to account/correct for the different quantities of Bi deposited on CPEs and CPμEs, as a result of different relative extents of hydrogen evolution and alkalization during the accumulation step, we have normalized the Pb and Cd stripping peak currents with respect to that of the corresponding Bi peak. This useful approach in SWASV at Bi electrodes, introduced by Wang and co-workers [11] to account for signal variations due to changes in mass transfer rate and deposition time, is based on the normalisation of the metal ion stripping current by the Bi stripping peak current. A constancy of this ratio implies a similar effect of these variables on metal and Bi deposition and most likely a constant deposit morphology and metal-Bi interactions too. We have used this parameter extensively to account for deviations from simple cases [7, 8, 10]. The effect of acetate concentration is obviously not a simple case, as argued above and as shown in Figure 5 below.

Unlike the picture of Figure 4, the patterns for both electrodes are now very similar. Once, the difference in Bi deposition charges is corrected for, both electrodes show a pronounced maximum at 0.01 M acetate (for all cases, apart from Cd at the CPE where this is slightly shifted to 0.02 M). This is because, in such a representation, the major parameter becomes the effect of acetate levels on the processes of deposition and striping of Pb and Cd alone, and this should be similar for both electrodes. At pH values below the $pK_a = 4.75$ of acetic acid [12] (such as those in solutions less than 0.1 M in acetate-see Table 1), most of the acetate is in its non-dissociated form (acetic acid) and hence the Pb and Cd speciation tends towards the free ion state. Because of the higher diffusion coefficient of the free ions, that in turn facilitates their deposition (during accumulation) and further increases the SWASV signal (by facilitating the reverse-redeposition step whose current is summed with that of the forward-stripping peak to give the SWASV signal).
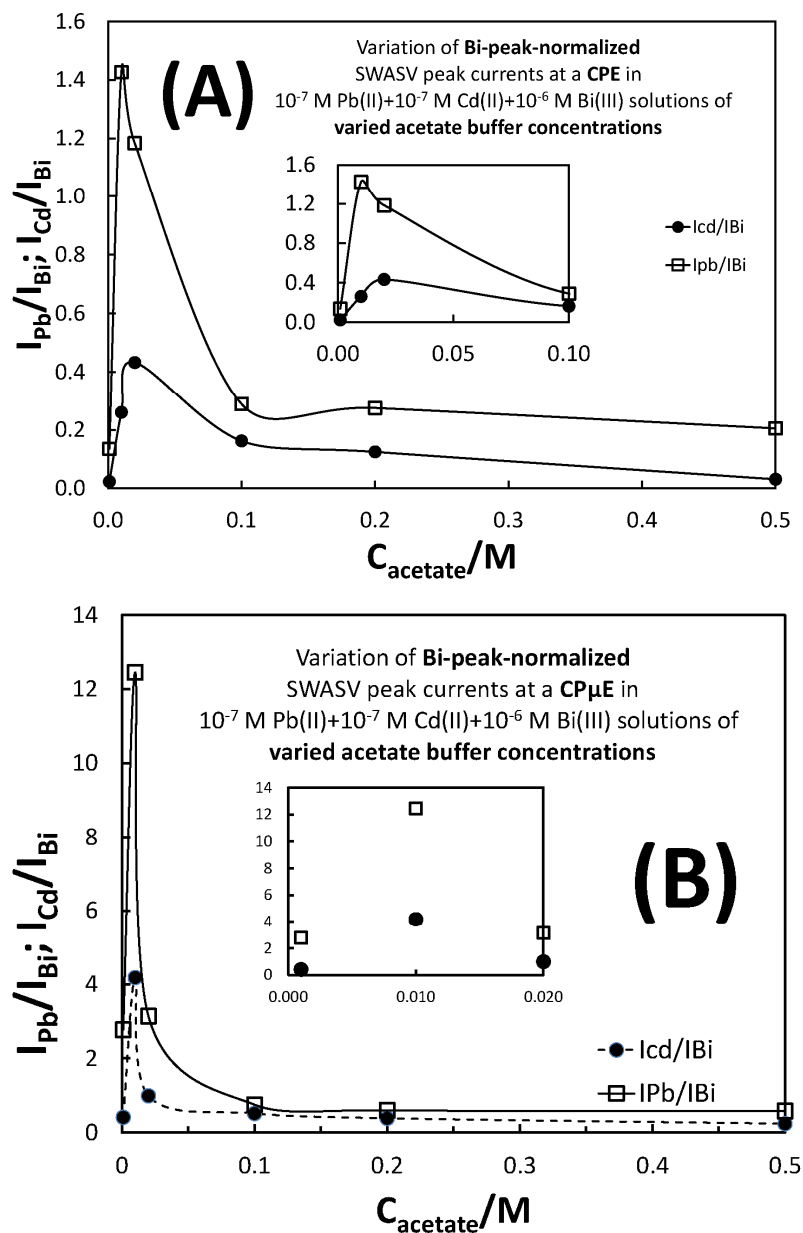
Fig. 5 *Normalised Cd and Pb stripping peak currents with respect to that of Bi, recorded at (A) a large CPE and (B) a small CPμE during SWASV experiments in Pb(II)+Cd(II)+Bi(III) as a function of acetate concentration in the 0.001-0.5 M range.*

Conclusions

i.   Due to their small total current, microelectrodes of the CPμE type make SWASV measurements in Pb(II) + Cd(II) + Bi(III) solutions of very low acetate levels (such as 0.001 M) possible; in such low conductivity media the quality of the response of conventional CPEs is rather low.

ii.   Due to high mass transfer rates (particularly relevant in the accumulation step), the SWASV response for all Pb, Cd and Bi metals is relatively higher at the CPμEs.

iii.   Due to decreased H_2 evolution during the accumulation step (a consequence again of high mass transfer rates of the metal ions), resulting in higher metal ion deposition current efficiencies and decreased alkalization of the electrode vicinity, CPμEs attain their highest Pb and Cd SWASV signal at the moderate-to-low acetate buffer concentration of 0.01 M.

Acknowledgements

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