POLAROGRAPHIC AND VOLTAMMETRIC BEHAVIOR OF THE ANTIBIOTIC CEFETAMET; REDUCTION OF THE METHOXYIMINO GROUP

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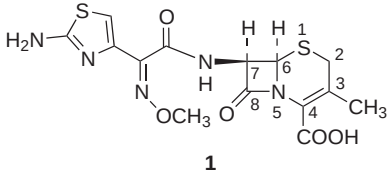
Evaluation of DC polarographic *i–E* curves and analogous curves obtained by cyclic voltammetry in aqueous buffers as well as in buffers containing 30% v/v ethanol indicated that the methoxyimino group of cefetamet is reduced on DME and HDME in the following way: the methoxyimino group can be at the electrode surface rapidly protonated up to pH about 9. In the protonated form of the grouping $(>C=NH–OCH_3)^+$, the OCH_3 is cleaved off in the first two-electron step. The resulting imine is in equilibrium with its protonated form, which is reduced in a second two-electron step. At pH higher than about 10, the unprotonated form of the methoxyimino group is reduced in a single four-electron step to amine. Studies using cyclic voltammetry were complicated by adsorption phenomena.

Keywords: Cefetamet; Cephalosporins; Oximino group; Electroreduction; Polarography; Voltammetry; Antibiotics; Electrochemistry.

Cefetamet (**1**) belongs among cephalosporins, a family of antibiotics with a broad spectrum of antimicrobial and antibacterial properties. They now often replace penicillins, as they have fewer side effects, for instance on the gastrointestinal tract. Cephalosporins contain a dihydrothiazine ring to which a β-lactam ring is fused. Most cephalosporins can be electrochemically reduced[1], either on the 3,4-double bond activated by the adjacent car-



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boxy group, or by cleaving a good leaving group R in the CH_2–R grouping on C-3. Numerous cephalosporins, including cefetamet (**1**) bear an electroreducible group in the side chain on C-7. In the case of cefetamet such reducible group is a methoxyimino group.

Hydroxyimino group (C=NOH) is well known to be reduced on mercury electrodes. It has been early observed[2,3] that the reduction occurs preferably on the protonated form and involves, under optimum conditions, transfer of four electrons, yielding an amine. As the rate of the protonation of the oxime decreases with increasing pH, above a certain pH is observed a decrease of the reduction wave with increasing pH. The plot of the decrease as a function of pH has a shape of a dissociation curve. Due to the rate of the re-establishment of the acid-base equilibrium in the vicinity of the electrode, the inflection point of the curve is observed at pH values that are several pH units higher than would correspond to the value of pK_a obtained at equilibrium.

If such re-establishment of the acid-base equilibrium takes place as a homogeneous reaction in a layer of solution in the vicinity of the electrode surface, the limiting currents in the pH range, where the current decrease is observed, would be independent of potential, as is the case with diffusion-controlled processes. The current–voltage curves of oximes show in the pH range where the wave-height decreases at a given pH a decrease in current with increasingly negative potentials[2]. This is an indication that protonation of oximes and their O-alkyl derivatives[4] occurs as a heterogeneous process. The oxime is adsorbed at the electrode surface and is protonated in the adsorbed state. As the adsorption, and hence the surface concentration of the hydroxyimino compound, decreases with increasingly negative potentials, the rate of protonation at a given pH decreases, and this results in a decrease in current with increasingly negative potentials[4]. The current at each potential (measured relatively to the half-wave potential) depends also on pH and the dependence has a shape of a dissociation curve. Such curves measured at varying potential are shifted along the pH axis. The pH at the inflection point of such curves depends on pK_a of the studied compound and on the rate of the protonation of the conjugate base. The shifts of these inflection points to a lower pH value with increasingly negative potentials are also a confirmation that the rate of protonation decreases with increasingly negative potentials[4].

Lund[5] first proved that the reduction of protonated forms of oximes and related derivatives of hydrazine occurs in two consecutive steps. Favored by the good leaving grouping character of –OH, –OR, $–NH_2$, NH_2R groups, the first two-electron step results in the cleavage of the N–O or N–N bond. Such

reduction generates an imine, which can be further protonated and reduced in a second two-electron step. In the majority of studied cases the potential of the reduction of imine in the second two-electron step is either similar or even more positive than that of the first reduction step of the oxime. Therefore, in the majority of cases the reductions of protonated forms of oximes[2,3,5] and their O-alkyl derivatives[4] take place in a single four-electron step. Initial studies of cefetamet (**1**)[6,7] indicated that its reduction differs from that of the majority of oximes, studied so far[8,9], in two aspects, which will be discussed in this contribution.

EXPERIMENTAL

Instrumentation

DC polarographic measurements were performed with a polarographic analyzer PAR 174A (Princeton Applied Research Corporation, U.S.A.). The three-electrode system involved dropping mercury electrode (DME) as a working electrode, a platinum spiral-shaped wire as an auxiliary electrode and saturated calomel electrode (SCE) as the reference electrode. The automatically controlled drop time of 1 s, scan rate of 5 mV/s and the mercury column height of 80 cm were used for polarographic measurements.

Voltammetric measurements were performed with an AMEL 433-A computerized polarographic analyzer. Three-electrode system was employed: static mercury electrode (drop size 40–80 arbitrary units) was used as the working electrode, and Ag|AgCl and Pt-wire as the reference and the auxiliary electrode.

The spectrophotometric measurements were carried out using a Beckman DU-650 spectrophotometer in a 1-cm quartz cell.

A Radiometer pH meter, PHM 220, with appropriate standard buffer solutions was used.

Chemicals

Cefetamet (**1**) sodium was donated by Hoffmann LaRoche (Basel, Switzerland). Materials for acetate, phosphate and borate buffers, methanol, ethanol, propan-2-ol, *tert*-butyl alcohol and acetonitrile were all p.a. quality (Merck, Darmstadt, Germany). Double distilled water was used throughout. All experiments were carried out at 25 °C.

Solutions

1 mM stock solutions of cefetamet (**1**) were prepared fresh daily in 0.2 M acetate buffer pH 4.6. Phosphate, acetate and borate buffers pH 2–12 were prepared either in water or in a mixture containing 30% v/v ethanol.

Procedures

To the electrochemical cell was transferred aqueous or 30% ethanolic buffer and deareated for 10 min using nitrogen. For polarographic measurements the stock solution of **1** was

added to make a final concentration of 0.2 mmol/l and the solution was purged with nitrogen for another 3 min and the current–voltage curves were recorded.

For voltammetric measurements the procedure was similar, but the final concentration of cefetamet (**1**) was 0.1 mmol/l.

RESULTS AND DISCUSSION

DC Polarography of Cefetamet

The dependence of polarographic limiting currents of cefetamet (**1**) on pH was followed in 0.02 mM solutions of **1** in aqueous buffers and in 0.2 mM solutions of **1** in buffers containing 30% v/v ethanol. In some aspects the variation of limiting currents with pH resembled those reported for the majority of other oximes[2–5]. In aqueous solutions the total limiting current of the four-electron wave, which corresponds to the reduction of the protonated form of the methoxyimino group, shows some variations (see below) between pH 2 and 8, but decreases with a further increase in pH. The plots of the dependence of the limiting current on pH have a shape of a dissociation curve (Fig. 1a) with an inflection point at pH about 9.5. In buffered solutions containing 30% ethanol the decrease of the wave of the protonated form is accompanied by an increase of the wave of the unprotonated form at more negative potentials (Figs 2a, 3). The behavior of **1** in DC polarography differs from that of majority of other oximes in two aspects:

1. In aqueous solutions the reduction wave I of the protonated form is – over a certain pH range – split into two Ia and Ib (Fig. 1, lit.[7]). The splitting is visually obvious at pH > 8, but using plots of $E = f[\log\{(i_d - i)/i\}]$ it can be distinguished already at pH > 5. The reason for this behavior has been discussed in detail elsewhere[7]. It has been concluded that the separation of the first two-electron wave of the reduction of the oxime yielding an imine from the second two-electron process corresponding to the reduction of the imine to amine is due to a difference in pK_a values of the oxime (3.1) and of the imine (about 4.2), as well as due to differences in $dE_{1/2}$/dpH slopes (Table I).

2. Contrary to other observations, the protonated form of **1** in aqueous solutions shows between pH 4.5 and 9 a limiting current significantly lower than would correspond to a four-electron diffusion-controlled process. The observed decrease (Fig. 1a) is attributed to covalent hydration, i.e. addition of water to C=N double bond[10]. The increase of limiting current with decreasing pH at pH below 6 corresponds to an acid-catalyzed hydration, the increase in the total current ($i_{Ia} + i_{Ib}$) with increasing pH between pH 8 and

9 is attributed to a base-catalyzed dehydration. The variability of the current between pH 3 and 8, showing no smooth curve on the $i = f(\mathrm{pH})$ plot may be attributed to contributions of general acid-base catalysis, but effects of buffer kind and concentration have not been followed in detail.

Plot of half-wave potentials, obtained in aqueous solutions, as a function of pH (Fig. 4a) shows several linear segments with varying slopes $\mathrm{d}E_{1/2}/\mathrm{dpH}$ (Table I), which indicate varying number of protons transferred before the potential determining electron transfer. Decrease in the slope at pH 8.0 indicates pH region, in which the pre-protonation becomes too slow relative

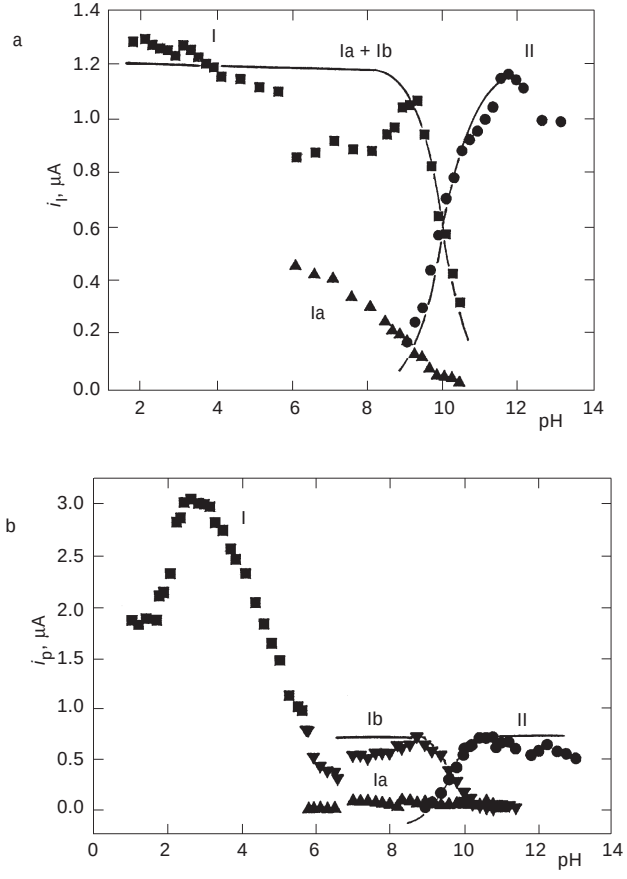

FIG. 1

Changes of currents with pH in aqueous solutions of buffers. a Dependence of limiting currents (obtained by DC polarography) of waves I (■), Ia (▲), Ia + Ib (at pH > 6) (■) and II (●) in solutions containing 0.2 mM cefetamet. b Dependence of cathodic peak currents (obtained by CV) of waves I (■), Ia (▲), Ib (▼) and II (●) in solutions containing 0.1 mM cefetamet

to diffusion. The half-wave potential of the unprotonated form (wave II) is, in accordance with theory, pH-independent, as the same species which predominates in the solution, undergoes also reduction. The shift of the half-wave potentials of wave II at pH > 11.8 is probably due to an addition of hydroxide ions.

In the presence of 30% ethanol (Figs 2a, 3) the limiting current i_I at pH < 9 is considerably lower than corresponds to a four-electron reduction. This is attributed to an addition of ethanol to **1**. Comparison with the four-electron diffusion-controlled reduction current of the unprotonated

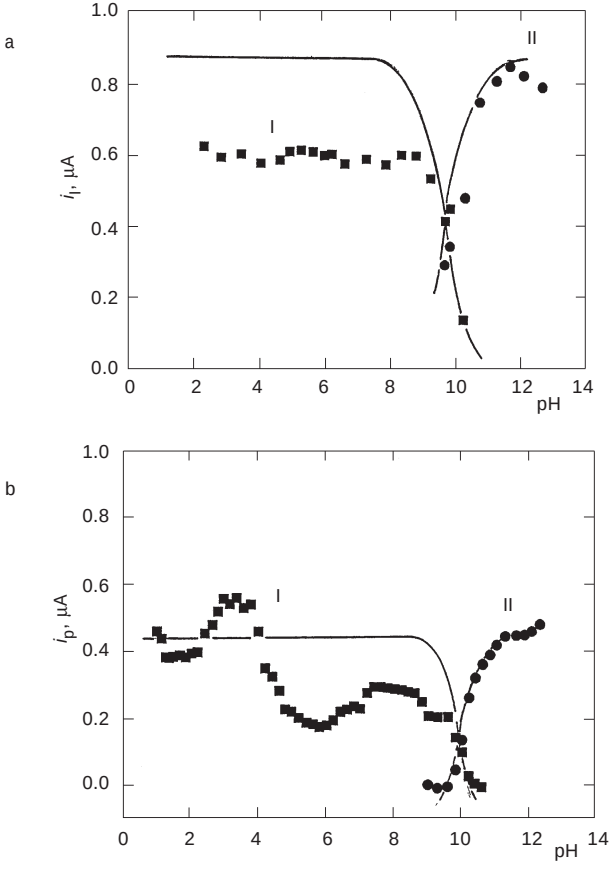

FIG. 2

Changes of currents with pH in buffered solutions containing 30% ethanol and 70% water. a Dependence of polarographic limiting currents of waves I (■) and II (●) in solutions containing 0.2 mM cefetamet. b Dependence of CV peak currents of waves I (■) and II (●) in solutions containing 0.1 mM cefetamet

form at pH about 11 indicates that in the protonated form of **1** at pH 2–8 about 30% of cefetamet (**1**) is present as an adduct with ethanol. The practical independence of wave i_I of pH in this pH range in the presence of 30% ethanol (Fig. 2a) is not caused by a larger shift of the equilibrium between **1** and the adduct in the presence of ethanol as compared with the corresponding equilibrium in the reaction with water, but due to a lesser effect of acid-base catalysis on the reversal of formation of the adduct.

In the presence of 30% ethanol the plots of half-wave potentials as a function of pH also show several linear segments (Table I). The intersection of two segments at pH 3.2, when the slope of the $E_{1/2}$–pH plot increases, is in good agreement the acid dissociation with pK_a 3.1 found spectrophotometrically[11], the intersections at pH 6.4 and 9.2, where the slope of the $E_{1/2} = f$(pH) plot decreases with increasing pH, correspond to a change in the rate of protonation in the vicinity of the electrode. The half-wave potential of the unprotonated form at pH 10.8 to 12.7 remains practically

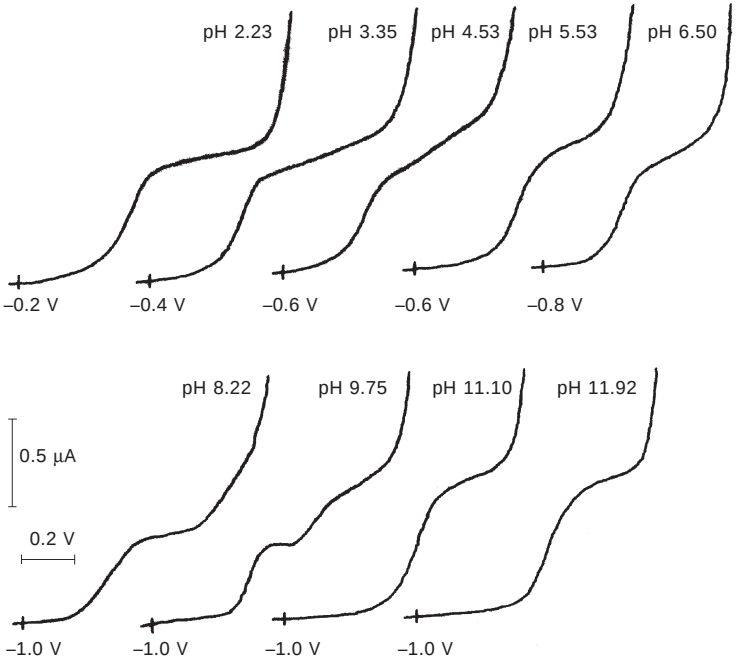

FIG. 3

Dependence of DC polarographic reduction waves of 0.2 mM cefetamet in the presence of 30% ethanol on pH. pH 2.2 $HClO_4$, pH 3.35–6.5 citrate buffers, pH 8.2 and 9.75 borate buffers, and pH 11.1 and 11.9 phosphate buffers. Initial potential indicated, capillary flow rate m = 2 mg/s, drop time t_1 = 2 s at mercury column height h = 80 cm

pH-independent (Fig. 4a), the small variations observed can be attributed to effects of cations of the supporting electrolyte, the concentration of which in buffers used has not been kept constant.

TABLE I
Shifts of half-wave (DCP) and peak (CV) potentials of individual waves of 2×10^{-4} M cefetamet in Britton–Robinson buffers (CV scan rate 100 mV/s)

Solvent	Technique	Wave	pH-range	d*E*/dpH V/pH
H_2O	DCP	I	1.7–5.0	0.056
		Ia	6.5–7.8	0.190
		Ib	5.8–8.0	0.135
			>8.0	0.000
		II	9–11.8	0.000
			>11.8	0.066
	CV	I	<1.6	0.000
			1.6–5.4	0.063
		Ia	7.0–10.3	0.100
		Ib	5.8–8.3	0.167
			>8.3	0.000
		II	<10	0.000
			10–13	0.044
30% EtOH,	DCP	I	2.0–3.2	0.000
70% H_2O			3.2–6.0	0.170
			6.0–9.0	0.084
			9.0–11.0	0.000
		II	10.8–12.7	0.000
	CV	I	1.0–3.5	0.000
			3.5–7.0	0.175
			7.0–9.0	0.070
			>9.0	0.000
		II	9.0–13.0	0.026

In attempts to study quantitatively the equilibria between **1**, water and ethanol (and other alcohols), the effect of increasing concentration of the alcohol was investigated in a mixture with water on the limiting current of the reduction of the protonated form of **1**. It was observed (Fig. 5) that the limiting current of **1** decreases with increasing concentration of alcohols, but slightly increases with increasing concentration of acetonitrile. This is in qualitative agreement with the effects of addition of water or alcohols. But limiting currents in such mixtures depend also on the relative viscosity of the solution, the diffusion-controlled currents being indirectly proportional to the square root of viscosity. When the currents given in Fig. 5 were multiplied by reliable values of square root of viscosity[12], the resulting corrected currents indicated qualitatively formation of adducts stronger than the adduct with water, particularly in the presence of propan-2-ol and *tert*-butyl alcohol. But the changes in limiting currents due to the addition

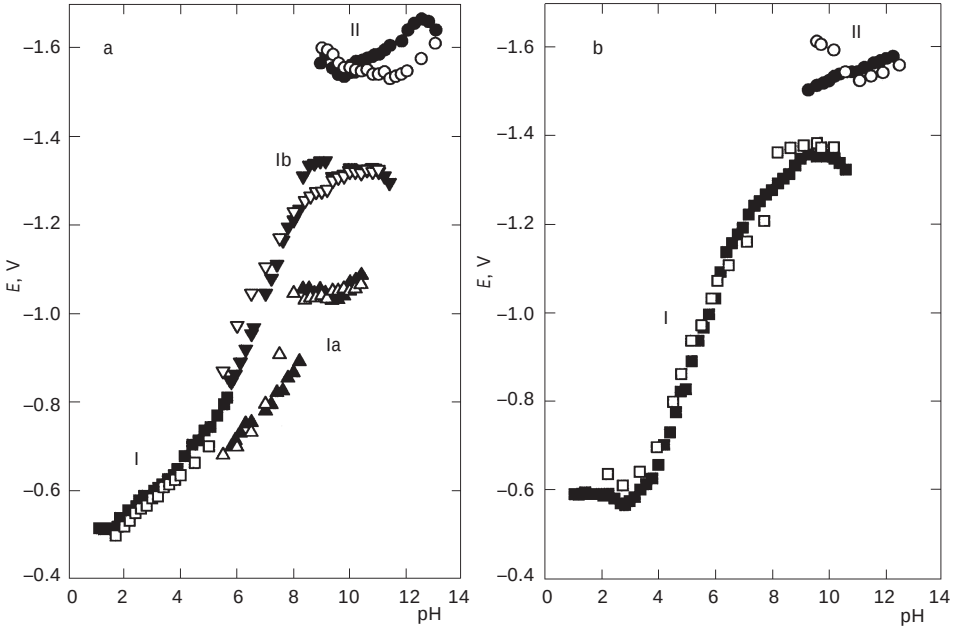

FIG. 4

Dependence of potential on pH in buffered solutions. a Aqueous solutions, polarographic half-wave potentials of waves I (□), Ia (△), Ib (△) and II (○) in solutions containing 0.2 mM cefetamet and CV peak potentials of waves I (■), Ia (▲), Ib (▼) and II (●) in solutions containing 0.2 mM cefetamet. b Solutions contaning 30% ethanol and 70% water, polarographic half-wave potentials of waves I (□) and II (○) in solutions containing 0.2 mM cefetamet and CV peak potentials of waves I (■) and II (●) in solutions containing 0.2 mM cefetamet

were too small compared to the changes due to variation in viscosity to allow calculation of reasonably accurate values of equilibrium constants for the addition reaction. The difference between the adduct formation with water and alcohols indicated relatively small differences between equilibrium constants for the addition of water and ethanol to compound **1**.

The formation of a covalent adduct has been supported by absorption spectra (Fig. 6). Increasing amount of water in an acetonitrile solution of cefetamet (**1**) resulted in a decrease of the absorption bands at 240 and 300 nm. 50% decrease has been observed in a mixture of 12% v/v water and 88% v/v acetonitrile, which corresponds to K_d = [unhydrated]/[hydrated form] about 7. This value, nevertheless, corresponds to an equilibrium in acetonitrile as a solvent and may be different from the value of such constant in water, due to differences in solvation of both forms involved.

Cyclic Voltammetry of Cefetamet

In aqueous solutions of **1** at pH 5.7–8.5 were observed two peaks of its protonated form (i_{pIa} and i_{pIb}). The sum of i_{pIa} and i_{pIb} reaches a value corresponding to a four-electron reduction at pH 8.7 (Fig. 1b). The lower value of this sum at pH 6 to 8.7 is attributed to hydration of the C=N bond, as

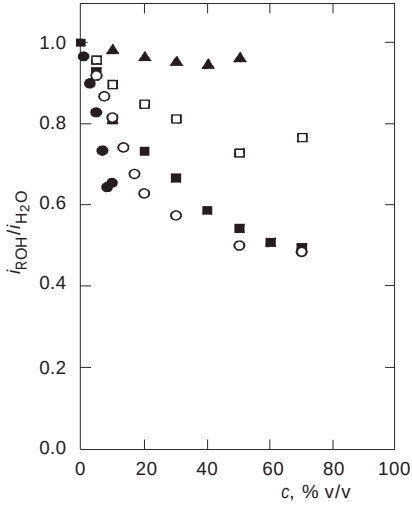

FIG. 5
Effect of addition of alcohols and acetonitrile on the limiting current of 0.1 mM solution of cefetamet in acetate buffer of pH 4.0. Concentration of the organic co-solvent given in % v/v. Acetonitrile (▲), ethanol (□), propan-1-ol (■), propan-2-ol (○), *tert*-butyl alcohol (●)

above. At pH > 8.5 the sum of peaks i_{pIa} and i_{pIb} decreases with increasing pH and the plot of the current as a function of pH has a shape of an dissociation curve with an inflection point at about pH 9.5, similarly as in aqueous solutions. When the rate of protonation decreases with increasing pH, these two peaks are gradually replaced by the peak i_{pII} at more negative potentials, corresponding to a four-electron reduction of the unprotonated form of **1**. The separate reduction of the N–O bond in oxime in i_{pIa} and of the C=N bond in resulting imine (which occurs at potentials where i_{pIb} is observed) is caused by differences in pK_a values of the oxime and the imine, and in values of d$E_{1/2}$/dpH, as discussed above.

The sharp increase in peak current i_{pI} with pH decreasing from 6 to 3 is attributed to a pH dependence of an adsorption–desorption process. With increasing pH the peak potentials of all these peaks were shifted to more negative values. As for polarographic half-wave potentials, the plots of the dependence of E_p on pH (Fig. 4a) consist of several linear segments with different slopes (Table I). The increase in the slope at pH 1.6 corresponds to the pK_a value of the protonated form. This value is significantly lower than the value 3.2 obtained in 30% ethanol, possibly due to a formation of adduct with ethanol and adsorption phenomena (see below). The pH independence of E_p of wave Ib at pH > 8.3 indicates absence of protonation between the first and second two-electron uptake. The four-electron reduction of the unprotonated form in wave II is affected at pH > 10 by addition of hydroxide ions, but the values of E_p in this pH range can be also caused by a double-layer effect, particularly dependent on concentration of cations of the supporting electrolyte, which have not been kept constant.

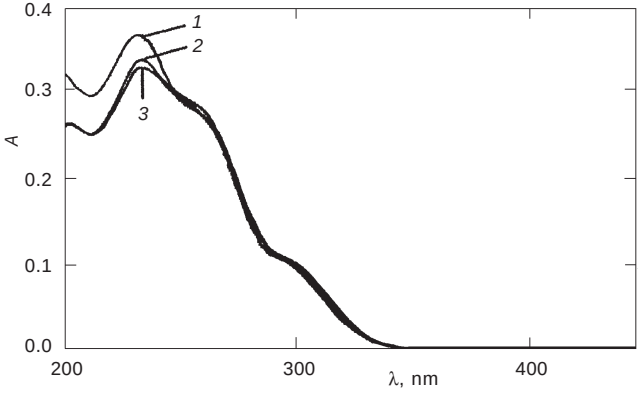

FIG. 6
Effect of water on UV-VIS spectra of 0.01 mM cefetamet in acetonitrile containing: *1* 5% v/v; *2* 20% v/v; *3* 50% water

In cyclic voltammograms obtained under all the above conditions, in the presence of peaks i_{pI}, i_{pIa}, i_{pIb} and i_{pII}, no anodic peak was observed at scanning rates varying from 5 to 1000 mV/s. This confirms the irreversible character of all reduction processes.

The considerable increase in current i_{pI} at pH < 4 above a value, corresponding to a four-electron, diffusion-controlled process, is attributed to adsorption–desorption processes. This was confirmed by the linear dependence of the peak current on the scan rate, discussed below. Adsorption of the protonated oxidized form of cefetamet at about –0.2 V is in agreement with the potential range in which oxidized forms of other cephalosporins were adsorbed at pH 0 and 4.7 [13].

In aqueous buffers containing 0.1 mM cefetamet, the peak i_{pI} at pH 2 to 4.6 was linearly dependent on scan rate (v), indicating that the peak current in this pH range is controlled by adsorption. Similarly the peak i_{pIa} at pH 8.5 and 9.5 was also governed by adsorption, but at pH 10.6 the current i_{pIa} was independent of v and hence controlled by the rate of chemical reaction (the protonation). Such currents are denoted as kinetic currents. Peak i_{pIb} at pH 7.2 and 8.5 was governed by adsorption, whereas at pH 9.6 it was a linear function of $v^{1/2}$ and thus diffusion-controlled. The peak i_{pII} of the reduction of the unprotonated form was diffusion-controlled over the pH range from 9.6 to 12.5.

In buffered solutions of cefetamet containing 30% ethanol, the patterns of variations of both peak currents (Fig. 2b) and peak potentials (Fig. 4b) with pH resembled those observed in aqueous buffers (Figs 1b and 4a), with two notable differences. In the presence of 30% ethanol only peaks i_{pI} and i_{pII} are observed. The peak i_{pI} is not split into two, due to a difference in the slope of $E_p = f(\text{pH})$ plots. Furthermore, the peak current i_{pII} is considerably higher than that of i_{pI}.

The slopes of linear segments of $E_p = f(\text{pH})$ plots are given in Table I. They resemble those obtained by DC polarography. The increase in slope of this plot at pH 3.5, which corresponds to the pK_a of the protonated form, is in good agreement with value 3.2 obtained by DC polarography. At pH about 9 the rate of protonation becomes unable to convert all the basic form of **1** (which predominates in the solution) into conjugate, protonated acidic form. This results in pH-independent values of peak potential of wave I at pH > 9.0. Smaller shifts of E_p of wave II at pH > 9 can be caused either by an addition of hydroxide ions to **1** or be due to a double-layer effect.

In mixtures of aqueous buffers containing 30% v/v ethanol at scan rates between 20 and 2000 mV/s, the peak current i_{pI} from pH 2 to 4.6 was controlled by adsorption, but between pH 5.6 to 9.6 by diffusion. When the

equilibrium in the latter pH range between the free and hydrated form is shifted in favor of the free form and, if in equilibrium more than 40% is present in the electroactive unhydrated form, dependence on scan rates does not allow to discern small contribution of the kinetic process to concentration of the predominant electroactive form. Hence these experiments do not allow determination of the equilibrium constant between the free and hydrated forms. Nevertheless, the *i–E* curves at pH 5.6 and 6.6 in 30% v/v ethanol as well as those at pH > 11.5 in aqueous buffers have a shape of a plateau rather than of a peak. This indicates participation of a chemical reaction in the electrode process.

The potentials E_p of peak i_{pI} in aqueous solutions at pH < 6 and in the presence of 30% v/v ethanol up to pH 9.6 were shifted to more negative potentials, at least up to 400 mV/s. Such behavior has been observed for numerous irreversible electrode processes. The potential of wave i_{pIa} in aqueous buffers pH > 8.5 remains practically independent of scan rate. The potential of the peak i_{pIb} in aqueous and of peak i_{pII} in the presence of 30% ethanol have shown only a slight dependence on the scan rate at v < 200 mV/s.

Reaction Scheme

On the whole, studies using CV on HMDE offered only a limited contribution, when compared with the information obtained by DC polarography. The main reason for limited use of peak currents obtained by CV are the more pronounced adsorption effects on the HMDE, in comparison with the behavior on DME.

Based on above evidence it is possible for the reduction of methoxyimino group in cefetamet (**1**) to propose the following reaction scheme.

$$>C=\overset{+}{N}H–OCH_3 \rightleftharpoons C=N–OCH_3 + H^+ \qquad (1)$$

$$>C=\overset{+}{N}H–OCH_3 + 2\ e + 2\ H^+ \longrightarrow >C=NH_2^+ + CH_3OH \quad i_{pIa} \qquad (2)$$

$$>C=NH_2^+ \rightleftharpoons >C=NH + H^+ \qquad (3)$$

$$>C=NH_2^+ + 2\ e + 2\ H^+ \longrightarrow >CH–NH_3^+ \quad i_{pIb} \qquad (4)$$

$$>C=N–OCH_3 + 4\ e + 4\ H^+ \longrightarrow >CH–NH_2 + CH_3OH \quad i_{pII} \qquad (5)$$

CONCLUSIONS

Compared to the reduction of other oximes reported in the literature[8,9], the protonated form of the methoxyimino group in cefetamet (**1**) is much more prone to the effects of the covalent addition of water and alcohols. This is manifested by a decrease in the limiting current of the protonated form of **1**, compared with a diffusion-controlled current of a four-electron reduction. The equilibrium between cefetamet and the hydrated form is relatively rapidly established; the dehydration of the adduct is acid- and base-catalyzed. The establishment of the equilibrium between cefetamet and alcohols is slower.

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