

Figure 3. Computed and measured electron density profiles for PVO orbit 422 and their comparison with VIRA model electron density profile. Computed vertical velocity gradient profile for PVO orbit 422 is also shown.

Table 1. Coronal holes (GSD 1980).

Date	Extent		Corresponding PVO orbit
	North	South	
26 Jan. 1980	+48° to -5°	-140° to +135°	417
31 Jan. 1980	+33° to +38°	-168° to +164°	422
2 Feb. 1980	+51° to +38° +21° to -43°	-143° to 160°	424

and proton flux on either side of the coronal holes. Considering the reported extent of these coronal holes and spiral motion of the solar wind, we find that the relaxation time of coronal transient is in conformity with several orbit duration of PVO at 0.7 AU as revealed by magnetic field variations shown in Figure 2, a and b. The continuous recording of solar wind velocity and proton flux also depict variations that may be caused by the presence of a coronal transient. We conjecture that this rare event was manifested by the coronal transient region lying in between the coronal holes which propagated and produced these unique variations in the measured electron density, magnetic field and inferred plasma transport velocity gradient during orbit 422 or PVO. This interpretation is of course speculative at present and implies that such coronal transients can originate in the region between coronal holes.

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## Differential pulse polarographic study of metal ion-tetracycline binding characteristics

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The complexation tendencies of the antibiotic tetracycline with the metal ions which neutralize its antibacterial effect have been studied in acidic and neutral aqueous solutions using differential pulse polarography. The results indicate that calcium(II) and magnesium(II) ions do not bind to ring A of tetracycline while aluminium(III) and iron(III) interact with a ring A at pH 4 as well as pH 7.

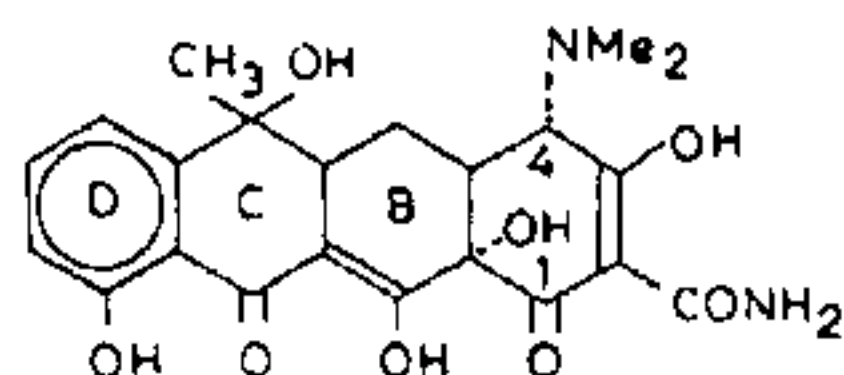
It has long been known that metal ions like  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  neutralize the antibacterial effect of tetracyclines on bacterial cultures<sup>1,2</sup>. Many techniques including spectrophotometry<sup>3,4</sup> NMR<sup>5</sup>, PMR<sup>6,7</sup>, potentiometric titrations<sup>8</sup> and circular dichroism<sup>9,10</sup> have been used to determine binding sites of tetracyclines with complexing ions but there is in general disagreement as to the specific site(s) of binding. However, it is clear that ring A plays a crucial part in complexation phenomenon.

On the basis of circular dichroism studies many workers have concluded that the BCD moiety binds at pH 5 and ring A binds at physiological pH only<sup>9-11</sup>.

Tetracycline (Tc) shows specific peaks in differential pulse polarography because of 4-dimethylamino function and keto group at position 1 in the ring A<sup>12,13</sup>, which is also believed to be involved in the complexation. Thus, differential pulse polarography (DPP) can provide useful information about binding of ring A with metal ions. This study was aimed to see (i) the effect of addition of various metal ions on the two DPP peaks of Tc to get information about the binding site(s) in ring A and (ii) the effect of pH on the binding of metal ions to Tc. The DPP behaviour of TcHCl in presence of metal ions like Ca<sup>2+</sup>, Mg<sup>2+</sup>, Al<sup>3+</sup> and Fe<sup>3+</sup> were examined at pH 4 and pH 7.

Tetracycline hydrochloride sample was the purest available from Sigma Chemicals and used as received. All other reagents were of Analaer grade and solutions were made in triple distilled water. Acetate buffer was used to maintain pH 4 and phosphate buffer for pH 7. Solutions were deoxygenated by purging argon for 15 min and polarograms recorded using a Tacussel PRG-5 pulse polarograph operating in a differential pulse mode with a pulse amplitude of 50 mV and scan rate of 2 mV/sec. The working electrode was a dropping mercury electrode with a 1-sec drop time which was controlled by a mechanical knocker, saturated calomel electrode was used as reference electrode and Pt-wire as auxiliary electrode. The capillary used had the following characteristics: in 0.1 M KCl at an open circuit the mercury flow was 0.8 mg/sec and natural droptime about 4 sec at  $h$  (uncorr) = 70 cm.

The structure of tetracycline is



Differential pulse polarogram of TcHCl (Figure 1, a) shows two major peaks, which are further subdivided, in the pH range 4-6. The first wave(s) has been attributed to reduction of 4-dimethylamino group resulting in deamination and the second to the reduction of keto group at C-1 in the ring A<sup>12,13</sup>. The results of addition of various cations on the DPP peak currents at pH 4 and pH 7 are shown in Figure 2. The DP polarogram of TcHCl remains unchanged with addition of even equimolar concentrations of Ca<sup>2+</sup> and Mg<sup>2+</sup> ions both at pH 4 and pH 7. This indicates that Ca<sup>2+</sup> and Mg<sup>2+</sup> do not bind to ring A of the TcHCl molecule at pH 4 as well as pH 7. This agrees well with the conclusion of Dolusio and Martin<sup>14</sup> on the basis of spectrophotometric data that 11,12- $\beta$  diketone in the BCD moiety is the binding site for Ca ions.

The effect of addition of Al<sup>3+</sup> to TcHCl at pH 4 was to markedly decrease the peak currents in the dp polarogram as shown in Figure 1. Jochsberger *et al.*<sup>15</sup> have also reported

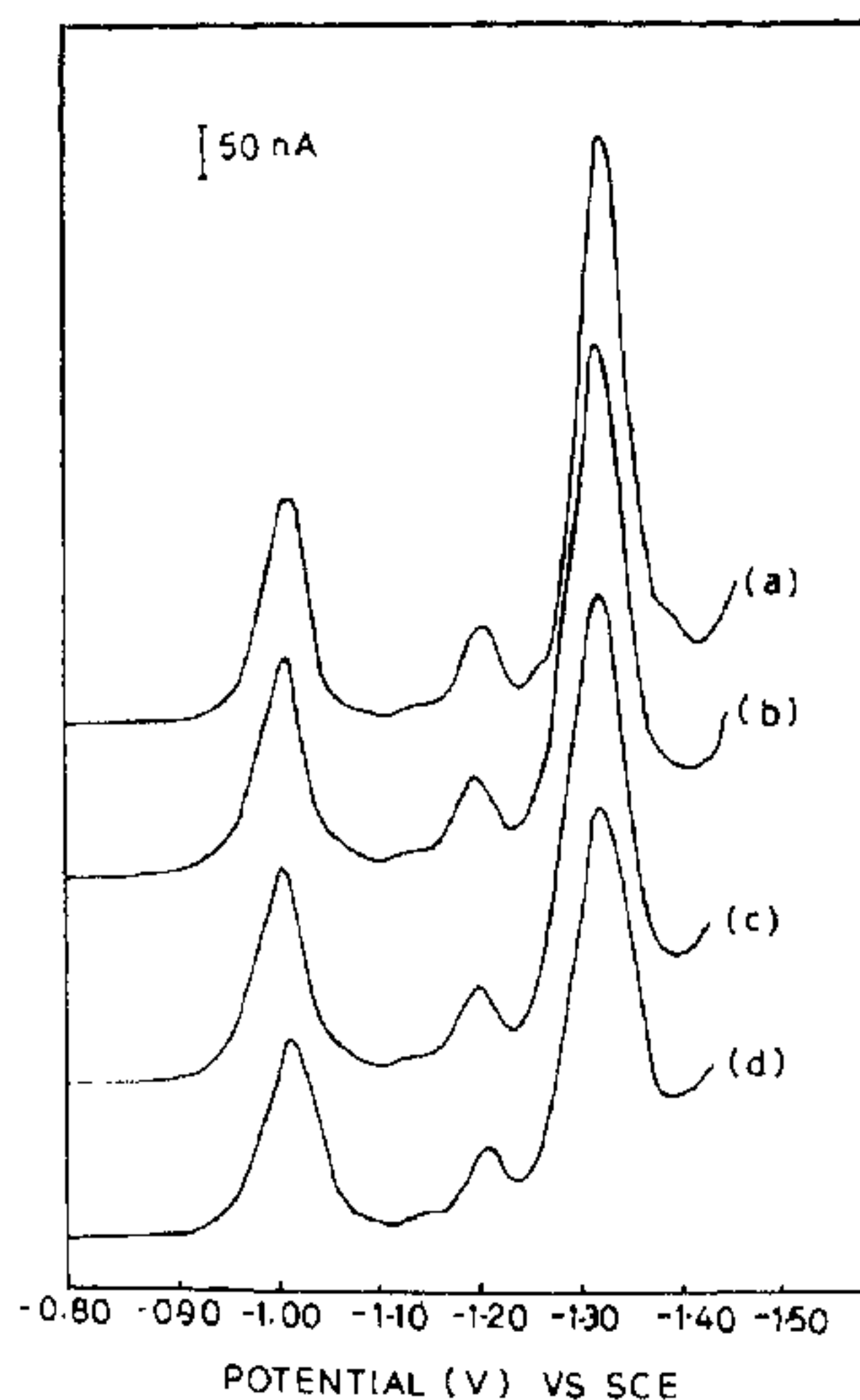


Figure 1. Effect of Al<sup>3+</sup> on the tetracycline hydrochloride polarogram ( $2 \times 10^{-5}$  M) at pH 4 in acetate buffer (a) TcHCl alone (b) TcHCl +  $5 \times 10^{-6}$  M Al<sup>3+</sup> (c) TcHCl +  $1 \times 10^{-5}$  M Al<sup>3+</sup>, and (d) TcHCl +  $2 \times 10^{-5}$  M Al<sup>3+</sup>.

the sharp decrease in the peak current of TcHCl at -1.35 V with the addition of Al<sup>3+</sup>. At pH 7, the addition of Al<sup>3+</sup> resulted in the decrease of both the peaks but the decrease was less pronounced than that at pH 4. As can be seen from the results, both at pH 4 and pH 7, the peak due to the reduction of C-1 keto group decreases much more than that due to the 4-dimethylamino function indicating that the Al<sup>3+</sup> interaction with the C-1 keto group is stronger than with the 4-dimethylamino group in ring A. That A-ring complexation does not involve the 4-dimethylamino function, but rather the carboxamido group and 1- or 3-enol has also been suggested by several other workers<sup>4, 16</sup>. The larger decrease in the peak currents at pH 4 than at pH 7 imply that the complexation of Al<sup>3+</sup> with the ring A is more at acidic pH than at neutral pH.

For Fe<sup>3+</sup> it was not possible to determine the interaction in the region -1.35 V due to the reduction of cation itself, thus the peak due to 4-dimethylamino function only was studied. The results again indicate interaction of Fe<sup>3+</sup> with ring A of the molecule at pH 4 and pH 7. Hence, these results are not in agreement with the circular dichroism studies conclusion that ring A binds at physiological pH only<sup>9-11</sup>. This difference may be due to the different conformations of tetracycline in acidic and neutral solutions<sup>17</sup>. At neutral pH, C<sub>12</sub>OH and C<sub>4</sub>NMe<sub>2</sub> groups in ring A are collinear and can easily get twisted upon binding with metal ions, resulting in conformational changes which

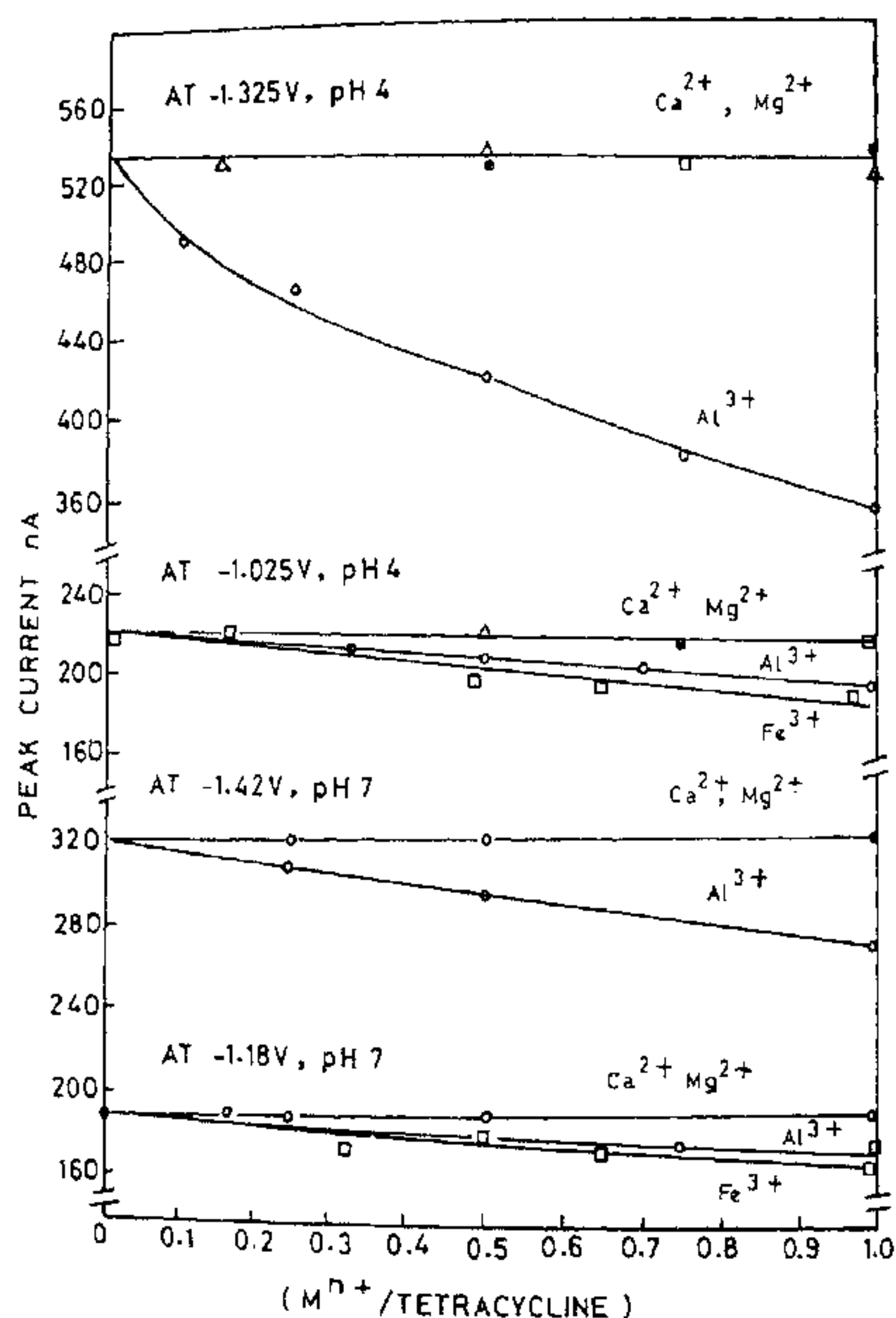


Figure 2. Effect of metal ions on the dpp peak currents of tetracycline hydrochloride at pH 4 (acetate buffer) and at pH 7 (phosphate buffer).

are reflected in circular dichroism spectra. In acidic solutions the ring A is already twisted and binding with metal ion may not result in conformational changes and thus no change in the circular dichroism spectra.

In summary, the DPP study results indicate that (i) Ca and Mg ions do not bind to ring A of Tc molecule, (ii)  $Al^{3+}$  and  $Fe^{3+}$  interact with ring A both at pH 4 as well as at pH 7, and (iii) for  $Al^{3+}$  the binding seems stronger at C-1 keto group in ring A.

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## Cretaceous/Tertiary boundary, iridium anomaly and foraminifer breaks in the Um Sohryngkew river section, Meghalaya

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The Langpar Formation of the Mawsmat type area in the Cherra plateau of Meghalaya contains a single foraminifer assemblage and diversity peak. Characteristic elements in the assemblage suggest a precise correlation between the type area and typical section of the formation in Um Sohryngkew river. The correlation brings out that: (i) the formation is restricted to the Palaeocene, and (ii) the underlying Mahadeo Formation in the Um Sohryngkew river section, referable mainly to the Cretaceous, is missing in the Cherra plateau due to a hiatus. Investigations on the microfaunal change close to the Cretaceous/Tertiary (K/T) iridium layer suggest existence of dwarfed and bored Cretaceous planktonic foraminifera in the Zone PO above this layer. The K/T planktonic extinctions in Meghalaya are not instantaneous. A leading role in their extinction was probably played by predator gastropod larvae.

THE Cretaceous/Tertiary (K/T) boundary and foraminifer taxonomy of 121 species from 73 samples of Mahadeo-Langpar-Therria Formations, exposed in the Um Sohryngkew river section were published about a decade ago<sup>1,2</sup>. The observed species distribution in the stratigraphic column is sufficient to construct a foraminifer diversity log of the Mahadeo-Langpar-Basal-Therria column (Figure 1). Such a log demonstrates that: (i) there are three Cretaceous-Palaeocene transgressions in the sequence with distinct peaks of foraminifer diversity, and (ii) a strong change occurs in Marine Transgression I at the K/T boundary. Investigations on the K/T change were also discussed<sup>3</sup>. A field trip was organized to show the K/T iridium layer to Acharya and Sen, who co-author a note<sup>4</sup>. Their note is based on: (i) an obscure illustration of a keelless