these esters[8,9] with the formation of benzyl ether as an intermediate. Although very little is known about the pyrolysis of these esters, it is evident that the borate and benzoate of this alcohol pyrolyse via different reaction pathways.

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## Polarography of Cadmium Transfusion – Gelatin Mixtures

PROTEIN solutions, generally used as maxima suppressors in polarographic work, are known to cause abnormal decrease in the diffusion current of metal ions due to factors such as adsorption[1,2], viscosity[3] and metal protein interaction[4–6]. The effect of increasing concentration of serum albumin on the limiting current of cadmium ion has been systematically investigated by Tanford[4], who explained the marked decrease in the current in view of cadmium-protein complex formation. Investigations in this direction have not, so far, been undertaken in the case of gelatin, although the latter has been most widely used as the maximum suppressor. To meet this end, transfusion gelatin, a modified product of bone gelatin, with its well-characterized nature (in terms of hydrogen ion equilibria[7] and mol. wt.[8]) was chosen and the effect of factors like *p*H, metal and protein concentration on the limiting current of cadmium was investigated.

Chemically pure samples of cadmium sulphate, potassium chloride, ammonium chloride, ammonia and transfusion gelatin (kindly supplied by the Director, National Chemical Laboratory, Poona) were used to prepare solutions in conductivity water and the metal content determined gravimetrically[9]. Ammoniacal as well as Walpole acetate buffers were made from 0·1 M solutions and their *p*H measured by Beckman *p*H meter model *G*. Polarographic measurements were carried out with a Fisher electropode in conjunction with a Multiflex galvanometer type $MGF_2$ in the external circuit, using an H-shaped polarographic cell[4], triply distilled mercury (for D.M.E.) and a water thermostat (Townson and Mercer, Croydon) maintained at 25° ± 0·1° C. Capillary characteristics determined by Lingane's method[10] were:

$m^{2/3}t^{1/6} = 1{\cdot}87$, $h = 52$ cm and length of capillary, $l = 15$ cm.

Nitrogen gas (purified by passing through alkaline pyrogallol and chromous chloride solution) was used to maintain the inert atmosphere. The diffusion currents were measured by extrapolation method. The mixtures prepared were: (1) containing 0·333 mM $Cd^{++}$, ammoniacal buffer (*p*H 9·6), potassium chloride (to maintain ionic strength, $\mu = 0{\cdot}15$) and varying concentrations of protein, namely, 0, 0·30, 0·40, 0·60, 0·65, 0·71, 0·75, 1·00, 1·20 and 1·35 per cent; (2) containing 2·5 per cent protein, buffer (*p*H 9·6) potassium chloride ($\mu = 0{\cdot}15$) and different concentrations of $Cd^{++}$ (2·664, 2·331, 1·998, 1·665, 1·332, 0·992, 0·666 and 0·499 mM); (3) containing 1·0 per cent protein, 0·333 mM of $Cd^{++}$, buffers of different *p*Hs 11·0, 10·0, 8·50, 6·8, 6·35, 5·95, 5·85, 4·50, 4·01, 3·80, 3·65, 3·00 and 2·65 and potassium chloride ($\mu = 0{\cdot}15$). A set similar to (2) was also prepared without protein. The reversibility of the waves was checked as described by Kolthoff and Lingane[3]. Values of diffusion currents, *id* and *ido*, in presence and absence of the protein are given in Fig. 1 (plots of *id/ido* versus *p*H, metal or protein concentrations). The limiting value of *id/ido* from the three curves (*A*, *B*, *C*) came out to be 0·73.

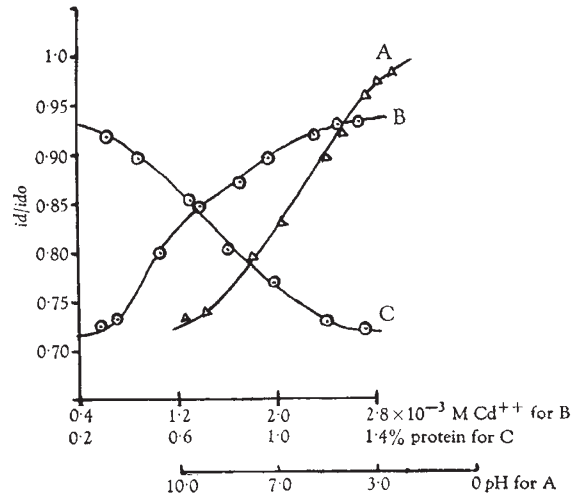


Fig. 1. Effects of *p*H, metal ion and protein concentrations on diffusion current depression. Curves *A*, *B* and *C* represent respectively the effects of *p*H, metal ion and protein concentrations on diffusion current decrease of cadmium ion at a total ionic strength of 0·15

From Fig. 1 it is evident that the ratio *id/ido* decreases with increase in *p*H and protein : metal ratios and attains a limiting value (not zero), showing thereby that non-specific forces like viscosity and adsorption are not responsible for the considerable decrease in the diffusion current in the case of cadmium. Therefore, the motal-protein interaction is the only way to account for these observations. Furthermore, the fact that it did not vary exactly as $\sqrt{h}$ shows that the limiting current is not entirely diffusion controlled[11] and a process slower than diffusion is involved in the reduction of cadmium ion bound to transfusion gelatin.

The values of $V_M$ calculated at different *p*Hs by the help of Tanford's equation were found to be approximately 2 at *p*H 8·5, where imidazole groups (in addition to carboxyl ones) offer principal sites[8] for metal ion binding. Since the value of $V_M$ at *p*H 5·8 is 1, it may be concluded that one cadmium ion is bound to the protein through its imidazole group. Similar results have been reported by Tanford[4] and Gurd[12] in the case of serum albumin. The value of log *K* calculated from Scatchard's[13] equation comes out to be 3·03 and $-\Delta F = 4{\cdot}118$ kcal/mole (at $Cd^{++}$ concentration 0·333 mM).

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