TABLE 1

No.	R=	R'	X	Transition temperatures °C	
				Nematic	Isotropic
I*a*	CH_3O	CH_3	H	129·0	274·5[3]
I*b*	CH_3	OCH_3	H	135·0	280·0
I*c*	CH_3	Cl	H	170·0	259·0
I*d*	CH_3	CH_3	H	170·0	240·0
I*e*	CH_3O	OCH_3	H	153·5	305·0[3]
I*f*	CH_3O	CH_3	OCH_3	(155·0)	185·0
I*g*	H_3CO	OCH_3	OCH_3	186·0	204·5
I*h*	H_3CO	Cl	OCH_3	(150·0)	170·0
I*i*	H_3CO	Cl	H	138·0	292·0

The reference to Table I shows that isomeric compounds I*a* and I*b* have nematic thermal stability difference of 5·5° C which may be due to the unsymmetrical linkage present in the molecules of I.

When two $-CH_3$ groups (I*d*) are replaced by two $-OCH_3$ groups (I*e*) in the system I, the nematic-isotropic thermal stabilities increase by 65° C. Now in the case of I*e* and I*a*, the $-OCH_3$ group from aniline moiety is replaced by $-CH_3$ group, the difference in nematic thermal stabilities is 30·5° C. If we consider the additivity of two such groups, the difference in the resultant compound should be of 61° C. Practically we have observed the difference to be 65° C. However, if we consider the replacement of $-OCH_3$ gsoup in (I*e*) by $-CH_3$ group on the ester side (I*b*) the difference of nematic thermal stabilities is of 25° C and if we consider the additivity of two such groups, it should be 50° C. This value is quite low compared to 65° C difference observed when two methyl groups are replaced by two methoxy groups in the system I. These observations clearly indicate that as the molecule is unsymmetrical and the exchanging groups have different polarity, the additivity in thermal stability is not observed in all the cases.

Introduction of lateral substituent like $-OCH_3$ group in (I*a*) decreases the nematic thermal stability by 119·5° C and the mesophase is rendered metastable (I*f*) whereas, in the case of (I*e*) introduction of the same $-OCH_3$ lateral substituent decreases the stability by 100° C and the mesophase is enantiotropic in nature (I*g*). In the case of compound (I*i*) the introduction of lateral $-OCH_3$ group renders nematic mesophase metastable and thermal stabilities are decreased by 142° C (I*h*).

These results suggest, even though the compounds have the same skeleton (type I) but having different end groups, the introduction of the same lateral substituent $-OCH_3$ does not have same detering effect. The decrease in thermal stabilities depend on the overall polarizability of the parent compound and the nature of the end groups.

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HABIT MODIFICATION CAUSED BY CHLORIDE IONS DURING THE ELECTRODEPOSITION OF SILVER FROM CYANIDE BATH ON SILVER (111) FACE

THE morphology of silver electrodeposits deposited on silver single crystals from argento cyanide bath has been studied by several workers to obtain brighter deposits[1-4]. The effects of phosphates, sulfates, chlorides and hydroxides have also been studied[5] on polycrystalline surfaces. However, very little work on the influence of chloride ions on the morphology of deposits grown on a flat single crystal substrate has been reported. The present experimental work was carried out to study the habit modification of silver electrodeposit, deposited on a silver (111) face from silver cyanide bath in presence of chloride ions.

The electropolishing was carried out as suggested by Shuttleworth, King and Chalmers[6]. The deposition was carried out at 2 mA/cm² and 5 mA/cm² on the (111) face from a solution containing 33·5 g of AgCN and 35 g of KCN and 38 g of K_2CO_3 in a litre of distilled water[7], to a thickness of 3·6 μ at 24° ± 2. A known amount of A.R. KCl solution was added whenever necessary. Fresh solutions were used for each experiment. The over-potential was measured with reference to a freshly prepared silver electrode using digital pH meter with an accuracy of ± 5 mV. The surface appearance was examined under phase

contrast microscopy and microphotographs were taken.

A polycrystalline deposit was obtained when silver was deposited from pure silver cyanide bath at 2 mA/cm² as noticed by earlier workers[6] (Fig. 1). The polycrystalline deposit slowly changed over to a dragged triangular pyramidal deposit when the added chloride concentration was 10^{-5} mol/l in the bath (Fig. 2). With further increase in the concentration of chloride ions to 10^{-3} mol/l a levelling of the deposit was observed (Fig. 3) and the deposit looks bright, with further increase of concentration of chloride ions there was reappearance of dragged pyramidal growth.

FIG. 1. Pollycrystaline deposit, when silver was deposited on (111) plane from pure cyanide bath at 2 mA/cm² (625 ×).

FIG. 2. Dragged Cony Pyramids of Silver when silver was deposited on (111) plane in presence of 10^{-5} mol/l of Cl^- ions at 2 mA/cm² (625 ×).

At 5 mA/cm² the deposit from pure bath was polycrystalline (*cf.* Fig. 1). At a concentration of 10^{-4} mol/l of chloride ions the grain size of the polycrystalline deposit was smaller. Further increase in the concentration to 10^{-1} mol/l, the deposit was bright and uniform.

The over-potential during deposition from pure cyanide bath remains steady with time. When the chloride ions are present the over-potential values will be higher than those from the pure solution (Fig. 4).

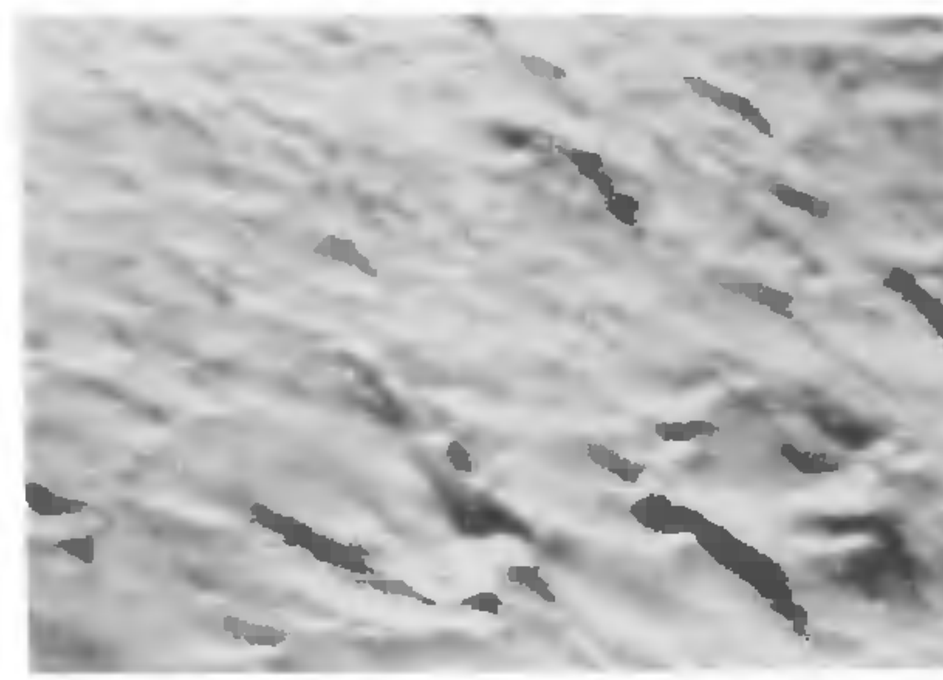

FIG. 3. Transition from cony pyramids to bright levelled deposit when deposited on (111) plane in presence of 10^{-3} mol/l of Cl^- ions from Argentocyanide bath at 2 mA/cm² (625 ×).

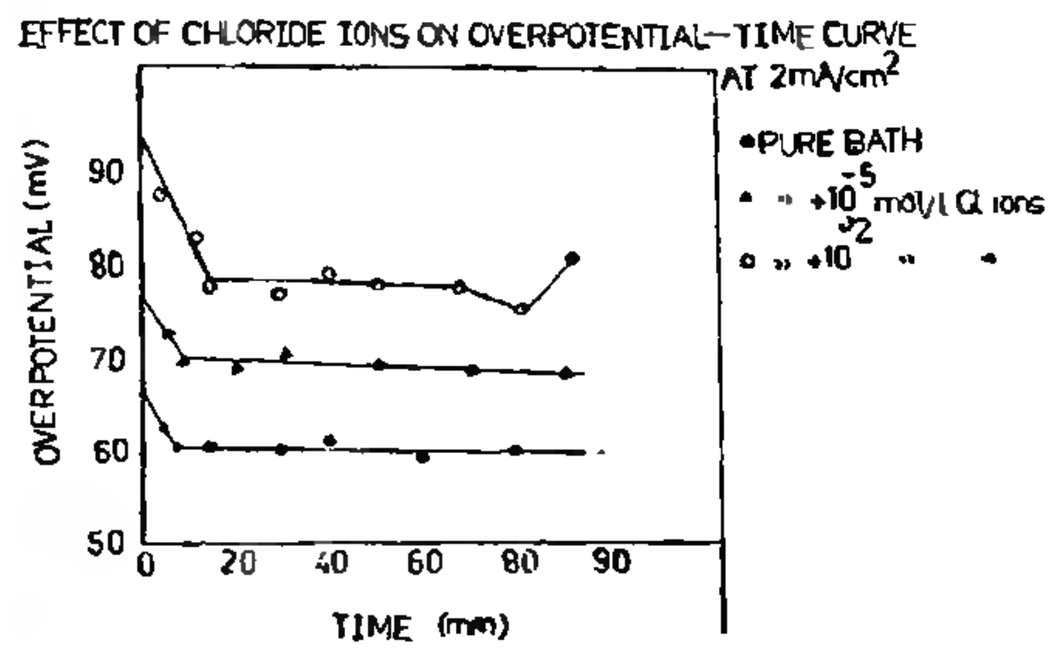

FIG. 4

The above results indicate the remarkable effect of chloride ions on the habit modification of silver electrodeposits from the cyanide bath and on the over-potentials during deposition. The presence of chloride ions in the bath may increase the stability of the complex and thus decrease the effective ion concentration in the bath. In the presence of the chloride ions, the ion transfer through the Helmholtz double layer may be retarded resulting in a growth habit modification and an increase in the over-potential. In addition to the above, there may be a possibility of the inclusion of AgCl in the deposit which can bring about the observed morphological change.

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ZINC(II) COMPLEXES WITH SCHIFF BASES DERIVED FROM SULPHONAMIDES

ZINC(II) complexes of the type ZnL_2 with Schiff bases (HL), derived from sulphonamides, *viz.*, sulphanilamide, sulphacetamide, sulphathiazole, sulphadiazine, sulphamerazine, sulphadimidine and $Zn(L) . H_2O$ from disalicylaldimine sulphaguanidine (H_2L) were prepared and characterised by elemental analysis, molecular weight determination, electronic and infrared spectra. The complexes have brilliant yellow colour and are insoluble in common organic solvents, soluble in dimethyl formamide and formamide, melt or decompose between 200–300° C, indicative of their polymeric nature, having tetrahedral or pseudo-octahedral stereochemistry with ligand chelating from the salicylaldimine part of HL or H_2L.

Introduction

The study of Schiff bases assumes considerable importance when complexed with metal ions. Literature survey[1,2] reveals that mostly solution studies have been carried out on Schiff bases, derived from sulphonamides in presence of metal ions. In continuation of our earlier work[3] on the complexes of certain transition metals with Schiff bases derived from some sulphonamides, we report hereunder Zinc(II) complexes with some of the Schiff bases similarly derived from sulphonamides, *viz.*, sulphanilamide (HSN), sulphacetamide (HSA), Sulphadiazine (HSZ), sulphamerazine (HSM), sulphathiazole (HST), sulphadimidine (HSD) and sulphaguanidine (H_2SG).

Experimental

Zinc(II) acetate (B.D.H.) was used as such for preparation of the complexes. Sulphonamides were obtained commercially and used as such after checking

TABLE I

Analytical and electronic data of Zinc(II) complexes of Schiff bases

Complexes and their colour	Mol. weight observed (theoretical)	decomp. point °C	Analytical data observed (Theoretical) %			Electronic spectral bands λ_{max} (mμ)
			M	N	S	
$Zn(SN)_2$ Brilliant yellow	569·8 (615)	240	10·24 (10·56)	8·79 (9·11)	10·28 (10·40)	220, 257, 300, 320, 435
$Zn(SA)_2$ Brilliant yellow	638 (699)	270	9·02 (9·29)	7·59 (8·01)	8·72 (9·15)	225, 252, 298, 320, 425
$Zn(ST)_2$ Brilliant yellow	715 (781)	272	8·13 (8·32)	10·27 (10·76)	15·99 (16·38)	220, 262, 295, 360, 435, 588
$Zn(SG) . H_2O$ Brilliant yellow	478 (503)	222*	11·28 (12·92)	10·82 (11·13)	6·16 (6·36)	218, 245, 262, 375, 475
$Zn(SZ)_2$ Brilliant yellow	719 (771)	280	8·16 (8·43)	14·12 (14·53)	7·95 (8·30)	235, 312, 415
$Zn(SM)_2$ Brilliant yellow	736 (799)	205*	7·98 (8·13)	13·67 (14·02)	7·77 (8·01)	248, 300, 400
$Zn(SD)_2$ Brilliant yellow	778 (827)	275	7·41 (7·85)	13·23 (13·54)	7·31 (7·73)	250, 287, 312, 400

* Melt with charring.