

Fig. 1 — Liquid crystalline behaviour of 4-*n*-alkoxy-1-naphthylidene-*p*-(*n*-amyloxy)anilines

the metastable modification C_{II} . The C_{II} modification is obtained by rapid cooling of the isotropic liquid phase. In the case of the C_2 -homolog both the solid forms give, on heating, the isotropic liquid which on cooling gives the monotropic nematic phase (Fig. 1a). In C_3 -homolog no nematic phase is observed (Fig. 1b).

The absence of liquid crystallinity in C_1 , C_3 - and C_5 -homologs may be due to the high melting points of these compounds. The melting points and transition temperatures of these compounds are lower compared with those of the corresponding benzylidene compounds studied by Dave and Patel⁴. Further work is in progress.

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Thiosemicarbazide as an Inhibitor in the Corrosion of Aluminium & Zinc

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The effectiveness of thiosemicarbazide as an inhibitor in HCl and NaOH for the corrosion of aluminium has been investigated. The percentage inhibition increases up to 87% in acidic solution at $[\text{inhibitor}] = 4.35 \times 10^{-3} M$. For the corrosion of aluminium, thiosemicarbazide (TSC) is a more effective inhibitor in acidic medium than in alkaline medium. This phenomenon has been attributed to the Zwitterion formation by TSC in alkaline medium. Similar behaviour is also observed for alkaline corrosion of zinc using TSC as inhibitor.

ORGANIC compounds are widely used as corrosion inhibitors^{1,2}. The mechanism of the action of such inhibitors depends on their molecular

structures³, molecular area⁴ and on their molecular weights^{5,6}. The activity of cations as corrosion inhibitors rather than the molecules, has also been considered⁷.

The activity of thiosemicarbazide (TSC) as an inhibitor in the corrosion of aluminium in both hydrochloric acid and sodium hydroxide solutions and of zinc metal in alkaline medium has now been evaluated.

Chemicals employed were of extra pure quality. The corrosion rate was determined using weight loss techniques. The percentage inhibition (P) was calculated from Eq. (1)

$$P = 100 (1 - W_2/W_1) \quad \dots(1)$$

where W_1 and W_2 are the corrosion rates in the absence and in presence of inhibitor respectively.

The rate of corrosion of aluminium is found to decrease with increase in $[\text{TSC}]$ in 1N hydrochloric acid and 1N sodium hydroxide solutions, similar to the behaviour that observed in acid corrosion of iron in the presence of TSC⁸. It was found that the change in the percentage inhibition is not appreciably affected and lies within the experimental error in the temperature range 24-30°. The percentage inhibition at $[\text{inhibitor}] = 4.39 \times 10^{-3} M$ is $\approx 87\%$ in HCl and 61% in NaOH solutions, the corresponding values for thiourea inhibition of aluminium corrosion are 60% and 16% respectively⁹. It can be assumed that thiosemicarbazide acts as a more efficient inhibitor than thiourea at the same concentration in both media.

Fig. 1 represents the corrosion rate of zinc against $\log [\text{inhibitor}]$ in 1N sodium hydroxide solution. As in the case of aluminium, the corrosion rate in the zinc metal decreases with increasing $[\text{TSC}]$. The more efficient inhibition exhibited by TSC as compared to thiourea is probably due to the additional $-\text{NH}-$ group in TSC molecule. Furthermore, the different charge distribution on TSC molecule increases its adsorption behaviour. However, due to the lower concentration of protons in alkaline medium, the inhibitor forms zwitterions⁹ which decrease the corrosion rate in alkaline medium as compared to that in acidic medium.

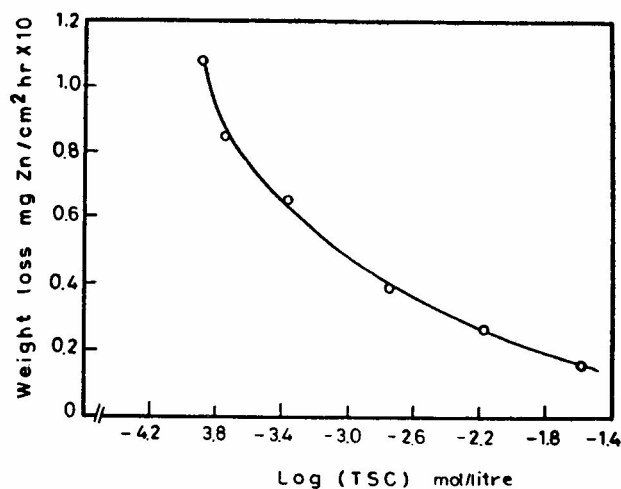


Fig. 1 — Effect of $[\text{thiosemicarbazide}]$ on the corrosion rate of zinc in 0.1N NaOH at 25°C

The applicability of Langmuir's equation to the adsorption of the inhibitor on the corroding surface was confirmed by the linear plot of $-\log [\text{TSC}]$ versus $\log p(1-p) \times 100$ in 1N NaOH at 30°. The deviation of the slope (0.42) of this plot from unity may be attributed to lateral interaction effects which are not considered in the equation.

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Heats of Solution of Mn(II), Co(II), Cu(II), Al(III), Fe(III), Ti(IV), Sn(IV), Sb(V), P(III) & I(III) Chlorides, Phosphoryl(V) Trichloride & Thionyl Chloride in Triethyl Phosphate

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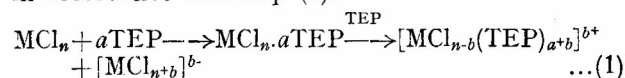
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The heats of mixing of Mn(II), Co(II), Cu(II), Al(III), Fe(III), I(III), P(III), Ti(IV), Sn(IV) and Sn(V) chlorides, phosphoryl(V) trichloride and thionyl chloride with TEP in dichloroethane have been measured calorimetrically. Attempt has been made to correlate these values with the ionization potential of the metal ions and $\nu\text{M-Cl}$ (far infrared).

MRYGINA *et al.*¹ determined the integral heat of mixing of chlorides of Ti(IV), Ge(IV) and Sn(IV) with tri-*n*-butyl phosphate for their 1:1000 and 1:500 mole ratios. Recently Gutmann and Czuba² have determined enthalpies of mixing of halides of As(III) and Sb(III) with tri-*n*-butyl phosphate in dichloroethane. But a detailed study has not been carried out in TEP. In this paper we report the values of heat of solution of some metal chlorides in TEP at different concentrations.

The reagents were purified as described earlier^{3,4}. An isothermal phase change calorimeter was employed for measuring heat changes using diphenyl ether as the dilatometric fluid. The variation in ΔH is of the order of ± 0.05 kcal/mole. The calorimeter was standardized and calibrated by titrating known amount of 0.01M NaOH against 0.01M HCl. The procedural details are described elsewhere⁵.

When metal chlorides dissolve in triethyl phosphate (TEP), a donor-acceptor complex between the solvent and the solute is formed as the first step which is followed by the ionization of the complex in accordance with Eq. (1).⁵

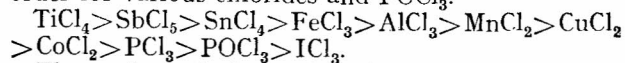


The heats of solution (ΔH) of the chlorides in TEP is given by Eq. (2) where ΔH_s represents enthalpy change due to solution formation including solvation, ΔH is the enthalpy change due to adduct formation and ΔH_i refers to enthalpy change due to ionization and subsequent solvation of the products.

$$\Delta H = \Delta H_s + \Delta H_c + \Delta H_i \quad \dots(2)$$

It has been assumed that at low concentrations of the solute the addition compound $\text{MCl}_n \cdot a\text{TEP}$ gets completely ionized and the measured enthalpy values more or less correspond to those for ionization of the metal chloride; at high solute concentrations, the ionization of the chloride becomes insignificant and measured enthalpy values largely correspond to ΔH_c .

Chlorides of Co(II), Mn(II), Cu(II), Sn(IV) and Ti(IV) form 1:2 adducts with TEP whereas Fe(III), Al(III), I(III) and Sb(V) chlorides give 1:1 adducts. For the estimation of ΔH_c the reactants have been taken in required ratios in CCl_4 (25 ml). In separate experiments heat of solution of TEP as well as of the solutes (SnCl_4 , TiCl_4 , SbCl_5 and PCl_3) in CCl_4 have been determined. Low experimental values (0.32-0.85 kcal mole⁻¹) suggest that dilution by CCl_4 does not affect ΔH_c significantly. ΔH_i has been determined from linear plot of measured enthalpy of reaction versus $[\text{solute}]^{1/2}$ in pure TEP. No adduct/ionization equilibrium has been envisaged. Thus ΔH_i corresponds to the value for extremely low concentration of the solute in extrapolated curve and ΔH_c pertains to the value of the required mole ratio of chloride/TEP. These values will include changes in enthalpy due to solvation, ΔH_s . During the enthalpimetric titrations (with and without the diluent CCl_4) the heat evolved has been found to increase with the amount of the solute. The linear curve could be extrapolated backward to almost zero concentration indicating that no side reaction is taking place. The values of ΔH given in Table 1 are in the following decreasing order for various chlorides and POCl_3 .



The order of decreasing ionization potential⁶, $\text{Fe}^{3+} > \text{Al}^{3+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+}$ shows marked correlation with order with respect to ΔH . The deviation in the correlation may be attributed to the fact that ionization potentials have not been corrected to correspond to a configuration $\text{M}(3d)^n(4s)^2 \rightarrow \text{M}^{2+}(3d)^n + 2e$ in TEP medium.

$\nu\text{M-Cl}$ (far IR) as also the ΔH_c (or ΔH_i) appear to depend on the oxidation state of the metal. ΔH (kcal mole⁻¹) values for chlorides of Mn(II), Fe(III), Sn(IV) and Sb(V) are 3.89 ± 0.1 ; 10.0 ± 0.2 , 12.53 ± 0.02 and 20.88 ± 0.22 respectively; corresponding $\nu\text{M-Cl}$ values also increase in the same order (the