

with total sulphur analysis using volumetric Carius method and with Kjeldahl total nitrogen determination.

The blank which accounts for the excess reagent to note the end point is about 0.1 ml for 30 ml titration solution. A convenient method to confirm the end point involves the addition of about 0.2 g of potassium iodide to the titrated solution and to note the relatively dark colour of iodine. Moreover, the intensity of iodine colour may be taken as a rough measure of the extent of over-titration. The titration should then be repeated by adding first all but 1 ml less of the previously required titrant and then dropwise with noting the colour of solution after each addition.

Large amounts (10 moles of substance added to each mole of sulphur containing amino acid) of serine, glycine and alanine do not interfere but tryptophan interferes severely even when present in small amounts.

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1. Berka, A., Vulterin, J. and Zyka, J., *Neuer Redox Titrants*, Pergamon Press, Oxford, 1965, p. 37.
2. Srivastava, A. and Bose, S., *J. Indian Chem. Soc.*, 1975, 52, 214.
3. Gowda, N. M. M., Murthy, A. S. A. and Mahadevappa, D. S., *Curr. Sci.*, 1975, 44, 5.
4. Mahadevappa, D. S. and Gowda, N. M. M., *Talanta*, 1975, 22, 771.
5. — and —, *J. Indian Chem. Soc.*, 1977, 54, 534.
6. Siggia, S. and Edsberg, R. L., *Anal. Chem.*, 1948, 20, 938.
7. Verma, K. K. and Bose, S., *Analyst*, 1975, 100, 366.
8. Thibert, R. J., Diederich, J. F. G. and Rutherford, K. G., *Can. J. Chem.*, 1965, 43, 205.
9. —, — and Kosicki, G. W., *Can. J. Biochem.*, 1967, 45, 1595.

### INTERACTION OF $\text{Li}^+$ AND $\text{NH}_4^+$ WITH ELECTRON DONOR MOLECULES

INTERACTION of alkali and alkaline earth metal cations with electron donor molecules like ethers, ketones and amides has been recently investigated in order to understand the nature of ion solvation<sup>1,2</sup>. Thus, studies of electronic spectra and molecular orbital calculations have shown that the binding of alkali metal ions with such oxygen donor molecules vary in the order  $\text{Li} > \text{Na}^+ > \text{K}^+$ . We considered it interesting to see whether  $\text{Li}^+$  binds to sulphur donors as well. Another aspect of interest was to examine the binding of  $\text{NH}_4^+$

to electron donor molecules. Such metal-ligand interaction studies are of relevance to biology<sup>3</sup>.

TABLE I  
CNDO/2 calculations on complexes of  $\text{Li}^+$  with oxygen and sulphur donors

1:1 Complex	X = O			X = S		
	$r, \text{\AA}$	$E_{\text{kcal}} / \text{mol}^{-1}$	$u, D$	$r, \text{\AA}$	$E_{\text{kcal}} / \text{mol}^{-1}$	$u, D$
$\text{H}_2\text{X}$	2.36	46	7.9	2.40	53	3.9
$\text{H}_2\text{CX}$	2.30	85	9.5	2.45	59	7.4
$\text{H}_2\text{NHCOX}$	2.30	116	9.5	2.40	79	12.3

CNDO/2 calculations were first made on the interaction of  $\text{Li}^+$  with a few sulphur donor molecules. The results show that  $\text{Li}^+$  binds quite strongly to sulphur donor molecules similar to oxygen donor molecules (Table I). On binding, the charge on the sulphur atom decreases, accompanied by a decrease in the positive charge on  $\text{Li}^+$ . In order to verify this conclusion from MO calculations, we examined the electronic spectra of a few compounds like ethylenetrithiocarbonate and thioformamide in presence of  $\text{LiCl}$  and found that the band due to the  $n-\pi^*$  transition of the  $\text{C}=\text{S}$  group is blue-shifted on binding with  $\text{Li}^+$ . This indicates that  $\text{Li}^+$  binds to the lone pair orbital of the  $\text{C}=\text{S}$  group. We then recorded the electronic spectrum of N, N-dimethylthioformamide (DMTF) in methanol with different concentrations of  $\text{LiCl}$ . The results shown in Fig. 1 clearly indicate blue-shift of the

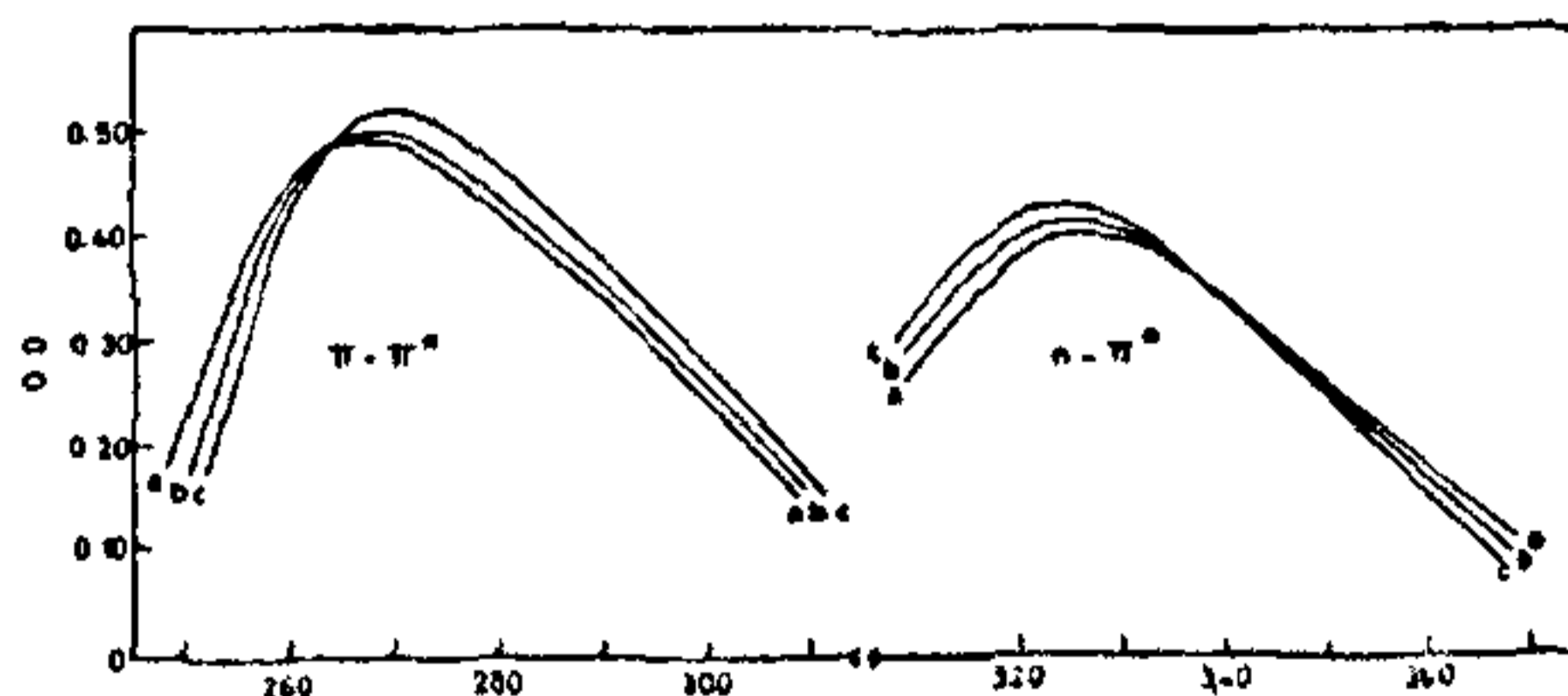


FIG. 1. Effect of  $\text{Li}^+$  on the  $\pi-\pi^*$  and  $n-\pi^*$  bands of DMTF in  $\text{CH}_3\text{OH}$  solution. Molarity of  $\text{LiCl}$  is (a) 0.0, (b) 2.0 and (c) 4.0. Concentration of DMTF is  $5 \times 10^{-5} \text{ M}$  and  $1 \times 10^{-2} \text{ M}$  for  $\pi-\pi^*$  and  $n-\pi^*$  bands respectively.

$n-\pi^*$  band and red-shift of the  $\pi-\pi^*$  band of the  $\text{C}=\text{S}$  group. More interesting is the occurrence of isosbestic points in the  $n-\pi^*$  and  $\pi-\pi^*$  bands around 338 and 264 nm respectively. The isosbestic points suggest the existence of equilibria involving the thioamide molecule. The nature of the solvation

equilibria would be similar to that described by Rao and coworkers<sup>1</sup>.

CNDO/2 calculations on the interaction of  $\text{NH}_4^+$  to electron donor molecules show the presence of definite interaction, although somewhat weaker than with  $\text{Li}^+$ . Electronic spectra of benzamide recorded with different concentrations of  $\text{NH}_4\text{Cl}$  in aqueous solution indicate increasing red-shifts of the  $\pi-\pi^*$  band at 225 nm and occurrence of an isosbestic point around 232 nm. The interaction is, however, much weaker than with  $\text{Li}^+$ . It appears that the trend for interaction of cations with electron donor molecules is,  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ \approx \text{NH}_4^+$ . An attempt was made to study the interaction of ammonium ion in non-polar solvents. For this purpose, we studied the interaction of tetraheptyl ammonium bromide with cyclopentanone in methanol employing the  $n-\pi^*$  band of the latter. Here again, there was some interaction, although very weak.

The present results establish that  $\text{Li}^+$  binds to sulphur donors and that  $\text{NH}_4^+$  also binds to electron donors. The latter result is consistent with the known coordinating ability of  $\text{NH}_4^+$  ion<sup>5,6</sup>.

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1. Rao, C. N. R., Rao, K. G. and Reddy, N. V. R., *J. Am. Chem. Soc.*, 1975, 97, 2918.
2. —, Randhawa, H. S., Reddy, N. V. R. and Chakravorty, D., *Spectrochim. Acta*, 1975, 31A, 1283.
3. Gupta, A. and Rao, C. N. R., *J. Phys. Chem.*, 1973, 77, 2889.
4. Rao, C. N. R., In: *Metal-Ligand Interactions in Biology*, Reidel Publ. Co., Dordrecht, Holland, 1976.
5. Williams, R. J. P., In: *Bio-inorganic Chemistry*, ACS Publication 100, 1971.
6. Poonia, N. S., *J. Inorg. Nucl. Chem.*, 1975, 37, 1859.

### EXTRACTION PHOTOMETRIC STUDY OF MANGANESE(II) AS SALICYLALDOXIMATE COMPLEX INTO *n*-BUTANOL

DETERMINATION of small amounts of manganese has become important in view of its use as an alloying element in many steels. Solvent extraction has proved very useful for the concentration and separation of manganese from other metals.

G. Gorbach *et al.*<sup>1</sup> reported that manganese(II) yields a brown complex with the oxime which could be extracted into chloroform. Ingvar Dahl<sup>2</sup> investigated the extraction of manganese with solution of salicylaldoxime in benzene.<sup>1</sup> The present communication describes the results obtained in the solvent extraction of manganese as its oxime with *n*-butanol. Butanol offers special advantages since the extract can be directly analysed polarographically.

#### Recommended Procedure

The extractions were carried out by shaking 10 ml of *n*-butanol with 10 ml of aqueous solution containing the oxime, the ammonia-ammonium chloride buffer (pH 9.2) and the metal ion ( $10^{-3}$  M) for about 10 minutes. The ionic strength of the aqueous phase was kept constant by adding sodium perchlorate solution (1.0 M). Quantitative extraction, as evidenced by the absence of polarographic wave for manganese in the aqueous phase, could be achieved within five minutes of shaking. The organic layer was separated and dried over anhydrous sodium sulphate and absorbance measurements were made, with ELICO SPECTROCOL model CL-23 (India). The extraction procedure was repeated with the aqueous solution devoid of the metal ion and the organic phase thus obtained is used as the solvent blank. Metal ion in the absence of the oxime gave no colour reaction. Polarography of this solution indicated no formation of Mn(III) in the alkaline buffer used in the studies.

#### Results

The maximum absorbance was observed at 420 nm. Hence the studies were carried out at this wavelength. The optimum pH for the extraction is found to be 9.2. A 10-fold excess of the reagent (oxime) is necessary for the rapid development of the colour. It is established from the Coleman's<sup>3</sup> plot that only a single species is extracted into *n*-butanol. The composition of the complex (1 : 1), obtained by Job's<sup>4</sup> method, is confirmed by log-log plot method. Beer's law is obeyed upto a maximum concentration of 16 ppm. The molar absorptivity and the Sandell's<sup>5</sup> sensitivity are  $3140 \pm 15$  litres mole<sup>-1</sup> cm<sup>-2</sup> and 0.0175  $\mu\text{g cm}^{-2}$  respectively. The standard deviation is 0.005. The stability constant of the complex calculated from the data obtained for Job's method is  $2.3 \times 10^5$ .

Zn(II) and Ni(II) do not interfere, more than 2-fold excess of Fe(III) interferes in the determination of manganese.

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